XV.—*Contributions to the Chemical History of Archil and of Litmus.* By ROBERT KANE, *M.D., M.R.I.A.* *Communicated by* FRANCIS BAILY, *Esq. V.P.R.S., &c. &c. &c.*

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AMONG the numerous and complex questions as to the constitution of organic substances, which have latterly attracted the attention of chemists, there is scarcely one possessed of more interest to the manufacturer, as well as to the philosopher, and the elucidation of which might better be expected to lead to improved processes in the arts, or to throw more light on difficult points of abstract theory, than the study of the nature and mode of origin of those remarkable colouring materials which form the basis of the archil and litmus of commerce, and which are obtained from lichens of various genera and species, themselves totally devoid of colour.

Although the problem of the origin and nature of these bodies has never been contemplated by chemists in the general point of view, by which alone consequent and satisfactory results could have been arrived at, yet from a very early period in organic chemistry, attention had been directed to isolated portions of it, particularly with regard to litmus, which from its general use as a reagent excited curiosity, and became the subject of frequent, though incomplete examination. Indeed, the nature of litmus appears to have been to many chemists peculiarly obscure, as notwithstanding the researches of FOURCROY and VAUQUELIN, of TENNANT, CHEVREUL, PERETTI, DESFOSSES, and many others, BERZELIUS declared in the last year that the chemistry of litmus remained yet to be created. Regarding archil, still less knowledge has been obtained. I am not aware of any writer who has occupied himself directly with its examination; and, indeed, it is only incidentally that HEEREN mentions, in his admirable memoir of the lichen products, any facts belonging to the substance found in commerce.

The origin of those beautiful colouring materials from the different kinds of colourless lichens has, however, formed the subject of extensive and connected investigation, for which we are indebted to HEEREN and to ROBIQUET; and it will be found useful in the subsequent portions of the present paper, to notice briefly the results to which those eminent chemists arrived. HEEREN analysed particularly the lichens *Parmelia Roccella*, and the *Lecanora Tartarea*. He found therein a peculiar body which he termed Erythrine, as being the basis of the red substances. This erythrine appeared by boiling in alcohol to be changed into another Pseudo-erythrine, and by exposure to the air, into a material soluble in water, which he called Erythrine-bitter. By acting on erythrine or erythrine-bitter with ammonia and exposure to air, there were produced in his experiments three substances, one, yellow, which he did not

further examine; the others, which are red, he termed lichen-red (Flechtenroth), and the wine-red, pigment; and, finally, he looked upon the lichen-red as being the colouring material of cudbear and of archil. It is unfortunate that this beautiful series of researches should have been left imperfect, indeed useless as regards the requisitions of organic chemistry at the present day, by there having been no attempt made to ascertain the composition of the numerous substances described by HEEREN, except two analyses by LIEBIG of small portions sent to him by HEEREN, one of the pseudo-erythrine, and the other of a peculiar acid, the roccellic acid, which was found in the *Parmelia Roccella*, but which was looked upon by HEEREN as distinct from those bodies which produce colour. These analyses, although, as might have been expected from the eminence of their author, quite accurate, yet from being isolated and uncontrolled by the analyses of the substances allied to pseudo-erythrine, have remained up to the present day without leading to any further progress in this promising and extensive field; and notwithstanding that there is little doubt of the phenomena having been described by HEEREN with care and exactness, we still remain in total ignorance of the organic changes which produce those phenomena, and of the laws of composition and of mutual reaction which characterize the various substances which he isolated and described. For the purpose, therefore, of establishing a theory of the production of lichen-red from erythrine, no materials whatsoever have been contributed by HEEREN.

The investigations of ROBIQUET have led to results which have been found of more direct utility, in illustrating the history of archil, than those of HEEREN. By analysing the *Variolaria dealbata*, ROBIQUET discovered therein a substance incapable of producing colour, which he termed Variolarine, and another matter of a saccharoid character, to which he gave the name of Orcine. By means of orcine, the red colour of the archil is produced; this substance ROBIQUET also isolated, and gave to it the name of Orceine. Not content with the isolation of these substances, and the description of the phenomena of their production and decomposition, ROBIQUET, and subsequently DUMAS, entered upon the analytical investigation of their constitution, in order to determine precisely the manner in which orceine is formed from orcine. The experimental results, however, were such as to admit of different formulæ being proposed, and hence new researches are necessary to ascertain whether the theory of DUMAS or that of LIEBIG, regarding the constitution of orceine, is most correct.

From the preceding sketch of what has been accomplished in this department, it is evident that, as far as concerns the higher objects of chemical investigation, nothing positive or fundamental has been done. Excepting the composition of orcine, no numerical result can be considered as fixed, and consequently no ground whereon to build a theory has been gained. But even in the mere qualitative part of the inquiry, very many questions arise, the solution of which is accompanied by great difficulty. What relation does orcine bear to the colourless substances described by HEEREN? In what relation do the orceine of ROBIQUET and the lichen-red of HEEREN stand? Do the various lichens contain the same colourless substances? or do they produce the

same ultimate coloured substance? These are questions which it will be at once seen all preceding researches leave quite untouched, and they must evidently be, at least in great part, solved before any considerable portion of light can be thrown upon this difficult part of science.

I do not pretend to have established in the present paper a complete solution of those difficult questions. In fact, months of continued investigation have proved to me, that the subject is still more complex than the statement above given would point it out to be. If my results appear to have placed the problem of the origin and constitution of these bodies in a more definite light than that in which it had previously been contemplated, and to have shown at least the difficulties of the subject, if not positively to have removed any of them, I shall consider the object for which I now submit to the scientific world these contributions to our knowledge in this department, as sufficiently attained.

The object of the present paper being threefold, viz. first, to ascertain the primitive form of the colour-making substance in a given species of lichen, and trace the stages through which it passes before the coloured substance is developed; secondly, to determine the nature of the various colouring substances which exist in the archil of commerce; and thirdly, the examination of the colouring materials of ordinary litmus; it will be found convenient to divide the paper into three sections under these three heads, and to treat of the subjects in the order above described. Through the kindness of a friend I was enabled to procure, in sufficient quantity, a lichen now used extensively in Liverpool in the manufacture of archil of a very superior kind; this lichen was ascertained by an eminent botanist to be the *Roccella Tinctoria*: it is imported from the Cape de Verd Islands, under the name of archil-weed, and generally sells for 200*l.* per ton: some specimens which I procured were of so fine a quality as to be valued at 320*l.* per ton. The archil and the litmus used in these researches were derived indifferently from various sources in Liverpool, London, and Dublin.

Section I. *Chemical Examination of the* Roccella Tinctoria (*Archil-weed*).

The treatment to which the lichen should be subjected in order to obtain from it the peculiar principles which it contains, I found after many trials, to be best arranged in the following manner. Having been first chopped very small, it is to be digested in successive quantities of alcohol kept just below boiling (about 140° Fahr.) for some hours, in a retort connected with a condensing apparatus, by which the vaporized portion of spirit may be collected and subsequently used. When by this means all matters soluble in spirit have been dissolved out, the solutions are to be united, and the spirit distilled off in a water bath, until the residue in the retort becomes dry. A mass of a yellowish colour is thus obtained. This mass is to be then boiled in water for a few minutes, and the liquor then filtered as rapidly as possible whilst very hot. What remains undissolved may be again treated by boiling in water, as long as any portion of it appears to dissolve.

The mass insoluble in water is next to be acted on by a weak solution of caustic potash at a temperature of about 100° of Fahr. until it ceases to dissolve. In general but a very small quantity of material remains behind. The alkaline liquor having been carefully filtered, is then to be rendered slightly acid by muriatic acid, a copious greenish yellow precipitate is produced, which must be collected and washed to remove all trace of acid. This substance is then to be dissolved in weak water of ammonia, and mixed with a solution of chloride of calcium in water; any precipitate which forms is to be separated by the filter, and the clear yellowish green liquors again treated by muriatic acid, by which the substance is precipitated, and having been freed from adhering traces of acid by careful washing, it may be considered pure. To this body, as being the origin of the coloured series, I have given the name of *Erythryline.*

The precipitate produced as above described with chloride of calcium, and which is generally formed but in exceedingly small quantity, is to be treated with dilute muriatic acid, which separates a white substance, identical, so far as the small quantity of it at my disposal allowed me to determine, with the *roccellic acid* discovered by Heeren and analysed by Liebig, but as its acid characters are not marked, I would propose for it the more appropriate name of *Roccelline.*

The watery solutions which had been obtained in the treatment of erythryline deposit, on cooling, beautiful crystals, having the appearance of boracic acid. The quantity of these crystals obtained depends on the manner in which the mass has been treated: if the boiling and filtration had been expeditiously carried on, the liquor often solidifies from the quantity of crystals which separate on cooling, but if the process had been slowly carried on, very little is obtained. These crystals having been removed, no more can be obtained by evaporating the liquors in which they had been formed, and if a liquor containing crystals be heated so that they redissolve, but very few again appear on the liquor being allowed to cool. This crystallized body, on examination, is found to be identical with the *pseudo-erythrine* discovered by Heeren and analysed by Liebig; but as it will be hereafter shown that this body is not the accidental product which Heeren considered it to be, but in reality one of the most important in the series, and that there is very great reason for supposing the *erythrine* of Heeren to have been a mixture of other bodies, I believe that I am justified in transferring to this body the name *erythrine,* as certainly the word *pseudo* was attached to it by Heeren under a misconception.

The watery solution, from which the crystallized erythrine has been deposited, is always more or less brown coloured. When evaporated in a water bath, it gives a semifluid brownish mass, which can scarcely be rendered quite solid by any temperature below that of incipient decomposition. The circumstance of this substance being formed from erythrine, its great solubility in water, and its peculiar bitterish taste, show it to be the erythrine-bitter of Heeren. This name, being well enough suited to our language, I shall retain.

When a strong solution of erythrine-bitter is exposed to the action of the air for

a considerable time, as, for some months, it is gradually converted into a mass of soft granular crystals, which by washing with strong cold alcohol may be obtained completely white. This crystalline material constitutes the last gradation in the series of bodies arising from erythryline, and as indicative of its position, I propose to distinguish it by the name *Telerythrine*. The word τελος indicating the termination, as the word υλη indicated the commencement, of the series.

There are thus found either pre-existing in the lichen *Roccella Tinctoria*, or produced immediately by the processes employed in its analysis, the following bodies:

1st. Erythryline.
2nd. Erythrine. Pseudo-erythrine of HEEREN.
3rd. Erythrine-bitter.
4th. Telerythrine.
5th. Roccelline, roccellic acid of HEEREN.

Generally speaking, these substances are identical with those found by HEEREN in the *Parmelia Roccella* and the *Leucanora Tartarea*; the ultimate production of telerythrine having escaped his notice, and, as I believe, his erythrine having been erythryline in an impure form mixed with other substances.

It is singular, however, that these substances are all different from those found by ROBIQUET in the *Variolaria dealbata*. I could not find in the lichen I examined a trace of variolarine or orcine, and certainly the Variolaria could not have contained either erythryline or erythrine without their having been recognized by ROBIQUET. We may consequently infer that there exist in the lichens which yield purple colours at least two groups, characterized by different active principles, but, as shall be hereafter shown, ultimately generating by their decomposition the same coloured substance; the archil from these various lichens being for the purposes of the arts identical, and containing in reality the same substance, orceine.

The lichen which has been exhausted by boiling alcohol and has furnished the substances above described, yields to boiling water only a small trace of starch and gummy matter. What then remains is merely woody fibre and some earthy salts.

I shall now proceed to the description of the properties and constitution of these substances in detail.

I. *Of Erythryline.*

This substance when first prepared, and particularly when the preliminary operations are rapidly conducted, is of a pale yellowish colour, often nearly white, which colour I consider, from the appearance of the plant, it should have if completely pure. It is more frequently, however, of a greenish tinge, arising, as I believe, from a very minute trace of chlorophyl, which attaches itself to it and accompanies it in all its reactions. From this trace of chlorophyl I do not know any mode of freeing it, but the quantity is so minute that I did not find specimens of erythryline of very different shades to differ from one another in composition in a greater degree than might and frequently does occur in different analyses of the same pure substance.

Erythryline is insoluble in water, cold or hot, but by boiling with water it is gradually altered, and the liquor is then found to contain erythrine-bitter. It is easily soluble in alcohol and in ether. It is soluble in alkaline liquors, from which it is precipitated on the addition of an acid. It combines with metallic oxides by way of double decomposition, forming salts or lakes, which are generally greenish coloured. It does not appear to possess acid properties, however; its alkaline solutions cannot be obtained in any form neutral to test paper; and I therefore think it better not to give to its name any form which acids are generally characterized by.

When heated, erythryline fuses a little above 212°, and on a further application of heat it is decomposed without any trace of tendency to volatilize.

Its analysis was effected as follows:

A. 0·358 gramme of material gave 0·878 gramme of carbonic acid, and 0·262 of water.

B. 0·407 gramme of material gave 0·987 gramme of carbonic acid, and 0·307 of water.

These results give the composition in 100 parts.

	A.	B.	
Carbon . . .	67·83	67·06	100·00
Hydrogen . .	8·13	8·37	
Oxygen . . .	24·04	24·57	

Leading to the formula $C_{22}\ H_{16}\ O_6$, which gives

22 Carbon . . .	134·2	67·71
16 Hydrogen . .	16·0	8·07
6 Oxygen . . .	48·0	24·22
	198·2	100·00

By mixing a solution of erythryline in ammonia, in which the alkali was as little as possible in excess, with a solution of nitrate of lead, and washing the precipitate until all impurities had been removed, there was obtained a pale greenish powder, which was dried at 212° Fahr. and then analysed.

A. 0·739 gramme of material gave by Berzelius' method 0·163 gramme of metallic lead, and 0·213 gramme of oxide of lead.

B. 0·710 gramme of material gave 0·811 gramme of carbonic acid, and 0·251 gramme of water.

The formula which results is $C_{22}\ H_{16}\ O_6 + 2\ PbO$. Thus

	Theory.		Experiment.
22 Carbon	= 134·2	31·85	31·58
16 Hydrogen	= 16·0	3·79	3·92
6 Oxygen	= 48·0	11·39	11·90
2 Oxide of lead	= 223·2	52·97	52·60
	421·4	100·00	100·00

It might appear much simpler to consider the formula of this substance as being but half of the above, $C_{11} H_8 O_3$, and the lead salt as $C_{11} H_8 O_3 + PbO$. But it will be seen that circumstances connected with the other substances of this series show that the equivalent contains the larger formula. A more important objection to which the formula just given is exposed, arises also from the constitution of many of the bodies to be afterwards described, that the number of equivalents of hydrogen is not sixteen but fifteen. The grounds of this supposition shall be hereafter noticed, and for comparison I will here insert the result calculated on that idea.

22 Carbon . . .	134·2	68·06
15 Hydrogen . .	15·0	7·60
6 Oxygen . . .	48·0	24·34
	197·2	100·00

The value of the carbon is but slightly altered, but the difference of hydrogen is very great; if the true value for hydrogen be fifteen atoms, then in one case there was 0·67 of hydrogen obtained too much. Notwithstanding this some may be inclined to adopt this number.

II. *Of Erythrine.*

This substance being the pseudo-erythrine of HEEREN, has been very determinately characterized by that chemist in his description of its properties. It is but very sparingly soluble in cold water; in boiling water, on the contrary, it dissolves in great abundance, and on cooling separates under the form of micaceous plates of considerable lustre. Its fresh solution in water is colourless, but if it be kept for a little time exposed to the air, particularly when hot, it rapidly becomes brown, still remaining, however, clear and transparent. The erythrine is then wholly, or in great part decomposed, and on cooling little or no deposition of crystals occurs.

Erythrine is very soluble in alcohol and ether; also in alkaline solutions, from which, however, it is precipitated unchanged on the addition of an acid. If its alkaline solutions be exposed to the air, they become coloured after a little time, brown with potash or soda, but wine-red if the alkali be ammonia.

At a temperature of about 220° FAHR., erythrine fuses without losing water. When further heated it is decomposed, giving the usual products of unazotized organic matter, without any portion being volatilized.

It does not precipitate any neutral metallic solution. If a solution of erythrine in ammonia be added to nitrate or acetate of lead, a copious white precipitate falls, which contains erythrine, and which was subsequently analysed.

To determine the composition of erythrine, the following analyses were made.

A. 0·428 gramme of material gave 0·947 gramme of carbonic acid, and 0·239 gramme of water.

B. 0·347 gramme of material gave 0·769 gramme of carbonic acid, and 0·194 of water.

From these results, the numbers which follow, and to which I will annex the result obtained by LIEBIG, with the specimen of pseudo-erythrine sent to him by HEEREN, are deducible, and they point to the very simple formula $C_5\ H_3\ O_2$, the calculated results of which are likewise added.

Experiment.	A.	B.	LIEBIG.	
Carbon . .	61·19	61·16	60·810	100·00
Hydrogen .	6·20	6·31	6·334	
Oxygen . .	32·61	32·53	32·856	

The theoretical numbers being,

5 Carbon . .	30·5	61·73
3 Hydrogen .	3·0	6·04
2 Oxygen . .	16·0	32·23
	49·5	100·00

The formula deduced by LIEBIG was almost identical, it being $C_{20}\ H_{12,5}\ O_8$.

The compound of erythrine with oxide of lead was found to give the following results.

A. 0·970 gramme gave 0·152 gramme of oxide of lead, and 0·585 gramme of metallic lead.

B. 1·088 gramme gave 0·468 gramme of carbonic acid, and 0·129 gramme of water.

The simplest formula expressing these results, is $C_5\ H_3\ O_2 + 2\ PbO$, which gives

	Theory.		Experiment.
5 atoms Carbon . .	30·5	11·18	11·89
3 atoms Hydrogen .	3·0	1·10	1·32
2 atoms Oxygen . .	16·0	5·87	6·20
2 atoms Oxide of lead	223·2	81·85	80·59
	272·7	100·00	100·00

The quantity of oxide of lead in this analysis varies more from the calculated result than in other cases it was found to do, the quantity of oxide of lead being generally between 81 and 82 per cent. The specimen analysed was prepared with as little alkali as possible, and hence probably a small quantity of erythrine in excess at once gave too high a value for the constituents of the organic element, and reduced the oxide of lead below the proper amount.

Although the very simple formula $C_5\ H_3\ O_2$, expresses so accurately the constitution of erythrine in its free as in its combined condition, yet some consideration is necessary before finally adopting it. The erythrine, as proved as well by the experiments of HEEREN as by my own, is but one member of a series of bodies arising from the erythryline, and hence there must be established formulæ, not merely exhibiting the numerical results of analysis, but also displaying the manner in which these bodies are produced, one from the other, before their history can be considered as complete. If we compare therefore the formulæ of erythryline and of erythrine as just now given,

$C_{22}\ H_{16}\ O_6$, and $C_5\ H_3\ O_2$, or $C_{20}\ H_{12}\ O_8$, there does not appear any very simple mode by which they can be connected, and I am consequently disposed to look upon the erythrine as containing in its equivalent the same quantity of carbon as exists in the erythryline, and assigning to it consequently the formula $C_{22}\ H_{13}\ O_9$, connected with that of erythryline by the substitution of three equivalents of oxygen for three equivalents of hydrogen. If erythryline be $C_{22}\ H_{15}\ O_6$, then erythrine will be $C_{22}\ H_{12}\ O_9$, to which, however, as will be seen from the annexed calculated results, the value of the hydrogen is not easily reconciled.

C_{22}	= 134·2	61·22		C_{22}	= 134·2	61·503
H_{13}	= 13·0	5·93		H_{12}	= 12·0	5·500
O_9	= 72·0	32·85		O_9	= 72·0	32·997
	219·2	100·00			218·2	100·000

On either of these formulæ the constitution of the lead salt agrees with experiments very satisfactorily; thus

C_{22}	= 134·2	12·05
H_{13}	= 13·0	1·17
O_9	= 72·0	6·47
8 PbO	= 892·8	80·31
	1112·0	100·00

The difference between 12 and 13 of hydrogen is here insensible.

It is an exceedingly interesting question to judge if the original erythrine of Heeren should be looked upon as a determinate and independent substance, or whether it should be considered as having been, under an impure form, any of the substances which I have found. The accuracy and detail with which Heeren operated upon the substances he describes, should certainly be considered as rendering it highly improbable that he could have examined his erythrine in such a variety of ways, without detecting it to be a mixture, if it really was so; and more, he assigns to erythrine two characters which certainly do not belong to either of the bodies which I have now described; 1st, that it is insoluble in ether; and 2nd, that when heated it is in part volatilized. On the other hand, if he had obtained the erythrine in a pure condition, it is not likely that he would have sent his pseudo-erythrine to Liebig for analysis, without sending also the substance, which was the far more important of the two, his erythrine; this point is strengthened also by the fact that he found the active principle of the *Lecanora Tartarea* to be by no means identical with, although strongly resembling erythrine. The conversion of his erythrine also into pseudo-erythrine by boiling with alcohol, indicates either the identity of erythryline with his erythrine, which can scarcely be supposed, or that his erythrine was a mixture of true erythrine with some other substances more sparingly soluble in alcohol and scarcely soluble in ether, which I consider to have been most probably

the fact. The difficulty might be got rid of, by supposing that the three lichens *Roccella Tinctoria*; *Parmelia Roccella*, and *Lecanora Tartarea*, all contained primitively different characteristic bodies, which possessed the common character of generating his pseudo-erythrine, and the bodies which result from its decomposition; but, although in a certain degree supported by the analogy of the *Variolaria dealbata*, which contains orcine and no erythrine, I consider this idea as being much less likely to be true, than that the erythrine of HEEREN should be found to have been a mixture. It is on these grounds that I have transferred the name erythrine to his pseudo-erythrine, the substance which has been just now described.

III. *Of Erythrine-bitter.—Amarythrine.*

The substance which I shall now proceed to describe, is that which forms when erythrine is dissolved in hot water and exposed for some days to the action of the air. Its existence was recognised fully by HEEREN, and I only propose the modification of his name as being in some degree more consonant to the principles of nomenclature in the English language.

The amarythrine has a very peculiar bitter sweet taste, which, as well as its odour, resembles that of burned sugar. It is exceedingly soluble in water, much less so in alcohol, and not at all in ether. Its affinity for water is such, that it cannot be obtained in a solid form without partial decomposition. Exposed in vacuo over concentrated sulphuric acid, it shows no tendency whatsoever to solidify, and remains in a stove at a temperature of 200° FAHR. for weeks perfectly liquid. If heated in an oil bath or over a lamp, the water may be expelled, but the brownish mass obtained is so evidently altered as to be unfit for analysis.

The solution of amarythrine in water is of a pale brown colour, perfectly neutral to test paper. With the ordinary metallic salts it yields precipitates, which are, when dried, of a reddish brown colour. The constitution of these salts is perfectly definite, and hence by means of them the composition of the amarythrine may be completely ascertained. The truly definite nature of the salts of amarythrine is fully shown by the fact, that the precipitate which first forms when a solution of nitrate of lead is precipitated by amarythrine, and the second portion which is produced when the acid supernatant liquor is neutralized by ammonia, were found to possess precisely the same composition. The amarythrate of lead was analysed as follows:

A. 0·491 of the precipitate formed by amarythrine in a solution of nitrate of lead, the liquor being acid, gave

0·208 of oxide of lead, and 0·015 of metallic lead.

0·565 of the same substance gave 0·569 of carbonic acid, and 0·151 of water.

B. 0·970 of the precipitate produced by neutralizing the acid liquor of A. gave 0·963 of carbonic acid, and 0·238 of water.

1·122 of the same substance gave 0·237 of oxide of lead, and 0·260 of metallic lead.

These substances had been dried at 212° in LIEBIG's drying apparatus with a current of air.

These results give the composition in 100 parts:

	A.		B.	
Carbon . . .	27·92	100·00	27·46	100·00
Hydrogen . .	2·96		2·72	
Oxygen . . .	23·50		23·92	
Oxide of lead .	45·62		45·90	

The simplest formula by which these results can be expressed is $C_{11}\,H_6\,O_7 + PbO$, which is very simply related to that of erythryline, $C_{11}\,H_8\,O_3$. To show, however, the connexion between erythrine and erythryline, the number of equivalents of carbon is taken as twenty-two, and then the origin of the amarythrine becomes extremely simple. The erythrine being $C_{22}\,H_{13}\,O_9$, the amarythrine is $C_{22}\,H_{13}\,O_{14}$, being formed by the absorption of five equivalents of oxygen. The calculated results of both formulæ are subjoined.

11 Carbon . .	67·1	27·88	22 Carbon . .	134·2	27·805
6 Hydrogen .	6·0	2·49	13 Hydrogen .	13·0	2·690
7 Oxygen . .	56·0	23·26	14 Oxygen . .	112·0	23·225
Oxide of lead	111·6	46·37	2 Oxide of lead	223·2	46·280
	240·7	100·00		482·4	100·000

Both agree well with experiment; the latter, however, best.

IV. *Of Telerythrine.*

When the semifluid amarythrine is exposed for a long time (several months) to the action of atmospheric air, it gradually changes into a mass of very minute granular crystals of a brownish yellow colour. These are very soluble in water, but less soluble in alcohol, by means of which they may, without much loss, be washed from adhering portions of unaltered amarythrine, and so obtained almost completely white. They can scarcely be purified by re-crystallization, as if re-dissolved in water the solution may remain for a long time before it again forms crystals. It is insoluble in ether.

The telerythrine is neutral to test paper. It combines with metallic oxides, forming precipitates which are very nearly quite white. Its taste is sweetish bitter. Ammonia acts on it much less rapidly than on the body last described, but ultimately the ammoniacal liquor becomes deep wine-red.

The following analyses were made of crystallized telerythrine dried carefully by pressure between folds of blotting paper, but without exposure to heat.

A. 0·506 of substance gave 0·819 of carbonic acid, and 0·172 of water.

B. 0·473 of substance gave 0·775 of carbonic acid, and 0·156 of water.

These results indicate the formula $C_{22}\,H_{10}\,O_{19}$, and give the per cent. composition, which, with the theory, follows.

	Theory.		Experiment A.	Experiment B.
22 Carbon .	134·2	45·31	44·79	45·35
10 Hydrogen .	10·0	3·37	3·78	3·67
19 Oxygen .	152·0	51·32	51·43	50·98
	296·2	100·00	100·00	100·00

These crystals were afterwards exposed to a current of dry air at 212° Fahr. in Liebig's drying apparatus, but did not lose any water.

To determine the constitution of the salts of telerythrine, the precipitate produced by it in a solution of sub-acetate of lead, having been dried at 212°, was analysed.

A. 1·180 gramme of material gave 0·691 of metallic lead, and 0·037 of oxide of lead.
1·982 gramme of same substance gave 1·097 of carbonic acid, and 0·230 of water.

B. Another portion was afterwards prepared by the same means: of it
1·124 gramme gave carbonic acid 0·628, and water 0·158.
1·162 gramme gave oxide of lead 0·127, and metallic lead 0·604.

These results lead to the formula $C_{22}\,H_9\,O_{18} + 5\,PbO$, and the composition per cent. is

	Theory.		Experiment A.	Experiment B.
22 Carbon . . .	134·2	15·88	15·29	15·46
9 Hydrogen . .	9·0	1·07	1·30	1·56
18 Oxygen . . .	144·0	17·04	17·22	15·94
5 Oxide of lead .	558·0	66·01	66·19	67·04
	845·2	100·00	100·00	100·00

The telerythrine is produced, therefore, from the amarythrine by the removal of four equivalents of hydrogen and the absorption in their place of four equivalents of oxygen; and the complete series of reactions which I have pointed out hitherto may be thus expressed:

$$
\begin{array}{ll}
\text{Erythryline . . .} & = C_{22}\,H_{16}\,O_6 \\
 & \quad - H_3 + O_3 \\
\hline
\text{Erythrine . . .} & = C_{22}\,H_{13}\,O_9 \\
 & \quad + O_5 \\
\hline
\text{Amarythrine . .} & \quad C_{22}\,H_{13}\,O_{14} \\
 & \quad - H_4 + O_4 \\
\hline
\text{Telerythrine . . .} & \quad C_{22}\,H_9\,O_{18}.
\end{array}
$$

In this manner it appears, therefore, that the changes in the constitution of the substances primitively existing in the *Roccella Tinctoria* proceed when exposed simply to the oxidizing agency of the air. In every one of these stages they are capable of

giving by treatment with ammonia the wine-red substance, which is the commencement of the archil series. It is, however, the amarythrine which most rapidly and most perfectly produces that result. The exact nature of the products of this interesting process will next be studied as they exist in the archil of commerce prepared from the species of lichen, the simpler changes of whose characteristic ingredients we have now examined.

Section II.—*Chemical examination of the* Archil (*Orseille*) *of Commerce.*

The archil which I made the subject of experiment, is prepared by treating in the usual manner by means of impure ammoniacal liquors, the lichen already described, previously ground down to a pulpy form. The complete production of archil requires considerable time, and indeed it will be hereafter shown, that archil is always in a transition from one stage to another, and that in these various conditions the nature of its colouring material is completely different.

To separate the substances contained in archil, the following process was ultimately found the most successful. A quantity of archil was rendered slightly acid by muriatic acid, and then evaporated cautiously to perfect dryness. The dry mass was boiled in spirit until this came off but very slightly coloured. The alcoholic liquors were then all mixed together and distilled in a water bath to dryness, by which a deep crimson mass was obtained. This was then powdered and washed with cold water until all traces of sal-ammoniac had been removed, the powder then dried and digested in warm sulphuric ether as long as this fluid became very sensibly coloured. After the action of the ether, the last traces of it having been removed by exposure to a temperature of 212° for a couple of hours, the proper colouring substance of the archil remains as a fine crimson powder. Of this substance there are two different modifications, of which one constitutes the orceine of ROBIQUET and DUMAS, and the other being very closely allied to it, I shall distinguish them by the terms *Alphaorceine* and *Betaorceine*, retaining the word *Orceine* as a kind of generic term for both.

The ethereal solutions, which are of a fine crimson colour, are next to be distilled in a water bath to dryness. A semifluid mass remains, of an oily nature, staining paper, and liquifying completely at a moderate heat. On standing for a few days, a little orceine gradually separates from it, and in order more certainly to free it from traces of that substance, it should be dissolved in the smallest possible quantity of ether, the solution decanted from the powdery orceine which remains undissolved, and then evaporated, at first at a very moderate heat, but ultimately being kept at 212° for a long time, in order to be certain that the last portions of ether had been expelled. The substance thus obtained is still not always simple, but the peculiar characteristics of it shall be hereafter described. I give to it the name of *Erythroleic acid.*

The mass which resisted the solvent action of the alcohol should next be boiled in water repeatedly. At first the liquor becomes pink from traces of orceine, which

the alcohol had not taken up. There then dissolves a substance which colours the water golden yellow, and there remains a dark red substance, apparently insoluble in water. The yellow colour imparted to the water cannot be due to any minute portion of this substance, for when the yellow liquor is evaporated, it leaves a film of solid material, which is not red, as should be the case, but yellow. The yellow substance is therefore probably a peculiar material, most likely the yellow material (gelbe materie) of HEEREN, but from the minute traces of it which I could obtain, I could not make any additions to its history further than that the alkalies did not appear to alter its colour. The substance insoluble in water has still to be separated from a quantity of vegetable fibre, arising from half decomposed shreds of lichen, and from some earthy matters with which it is mixed. For this purpose it is to be boiled with a weak solution of caustic potash, in which it rapidly dissolves. The solution is wine-red coloured, without a shade of purple. On neutralizing the solution by an acid, there does not take place any precipitation; but if the solution be then evaporated to dryness, and then washed until all the salt of potash is removed, the substance remains pure, as far as the experiments I have instituted with it could indicate. To this substance, from considerations which will hereafter appear, I give the name of *Azoerythrine*.

The archil of commerce is thus found to consist essentially of three ingredients, orceine, erythroleic acid, and azoerythrine; of each of the two former there exist two modifications, which will shortly be described; and there is in addition, the yellow matter. It is important to determine now, how far these results agree with those obtained by HEEREN, in examining the products evolved by his erythrine in contact with air and with ammonia.

1st. In all properties given by HEEREN, his lichen-red (flechtenroth) identifies itself with orceine.

2nd. The azoerythrine assimilates itself to the wine-red pigment of HEEREN, in the characteristic property of not being coloured violet by alkalies. He appears, however, to consider the wine-red pigment as being soluble in water, whilst in reality it is its combination with an alkali that is so. As he operated on a solution in ammonia, there is every reason to look upon the substances as identical.

3rd. The yellow substance is mentioned by HEEREN only incidentally, and no comparison can be instituted.

4th. HEEREN did not meet with the erythroleic acid; indeed, operating on erythrine, he could not meet with it, as it shall be hereafter shown to have its origin in a substance of a totally different nature.

The researches of HEEREN, having thus to a great extent anticipated my results as to the constitution of archil, it may be necessary for me briefly to justify the change that I have made in his nomenclature. The word lichen-red would be certainly a much better name for that substance than orceine, since orcine is not the only primitive material capable of yielding it; but the word Orceine has become by the

labours of Robiquet and Dumas so fixed in scientific language, that very few persons would go back to lichen-red, which in addition does not adapt itself so well to the structure of English or French nomenclature as orceine. The word wine-red pigment is one which could not conveniently be retained in any scientific language; it is totally unfit for expressing the classes of compounds which this substance forms; and as I shall have occasion soon to show that this body is connected in a very interesting manner with the erythrine series, the name azoerythrine appears to me one of the least objectionable possible.

In analysing the substances of this group which contain nitrogen, the usual precautions were taken to avoid the source of error arising from the formation of nitric oxide. In every instance, three inches of the anterior of the tube were occupied by clean metallic copper, in the form either of thin sheet clippings, or coarse powder freshly reduced by hydrogen. In other respects, the analyses were conducted in the manner which has been already described.

I. *Of Azoerythrine.*

Although at first sight there appears to be a considerable quantity of the solid material of archil insoluble in spirit, yet when the process already described has been followed out, the portion of pure azoerythrine is found to be exceedingly minute, so that it is necessary to operate upon a considerable quantity of archil in order to obtain sufficient for the purpose of analysis. As prepared from different portions of archil, however, its properties appear to be sensibly the same.

These properties may be deduced in great part from what has been already said. Insoluble in water, in alcohol, and in ether, it dissolves in alkaline liquors, giving the characteristic port wine colour. This solution is not precipitated by acids. With solution of acetate of lead and other metallic salts it gives brownish red precipitates. Heated, it gives water and other pyrogenic products, but neither melts nor does it volatilize; nor was I able to detect among the products of the action of a moderately high temperature upon it, any orceine, as should be found according to Heeren's statement, that his wine-red pigment, when heated, gives off a vapour free from azote, and produces lichen-red. The quantity of material at my disposal was however so very small, that I do not at all consider Heeren's statement as being destitute of truth.

The analysis of this substance is liable to difficulty, on account of the possible existence in it of traces of another substance, equally insoluble in alcohol, and very sparingly soluble in water, and which, although properly a constituent of litmus, yet occasionally is to be found in archil, although in very minute quantity. This foreign substance (azolitmine) which shall be hereafter described, is turned blue by alkalies, and hence whenever the alkaline solution of azoerythrine possesses any slight bluish or violet tinge, it may be inferred to be contaminated by the presence of azolitmine, and consequently unfit for being used for obtaining numerical results.

A specimen of azoerythrine, which I had every reason to look upon as being completely pure, was analysed.

0·300 gramme of substance dried at 212° gave 0·421 gramme of carbonic acid, and 0·154 of water.

To determine the quantity of nitrogen, the method of estimating the relative volumes of the carbonic acid and the nitrogen gases was adopted, in preference to the method of absolute determination, because I was perfectly certain of the relative accuracy of graduation of the tubes which I employed, but I could not be so certain of their absolute exactness. The following numbers express the result of an experiment of this kind, made with every precaution for avoiding error.

Tube.	$CO_2 + N$.		N.		CO_2.		N	:	CO_2.
A.	464	gave	21	and	443.	∴	1	:	21·1
B.	205	gave	9	and	196.	∴	1	:	21·8
C.	242	gave	11	and	231.	∴	1	:	20·0
D.	359	gave	17	and	342.	∴	1	:	20·1

In an experiment of this kind all sources of error tend to increase the quantity of nitrogen in relation to the carbon, and hence I consider the numbers above given as rendering it highly probable that the true proportion is one of nitrogen to twenty-two of carbon, and on this idea the analysis leads to the formula $C_{22}\,H_{19}\,N\,O_{22}$, giving

	Theory.		Experiment.
22 Carbon . .	134·2	39·09	38·80
19 Hydrogen . .	19·0	5·53	5·70
22 Oxygen. . .	176·0	51·27 }	55·50
1 Nitrogen . .	14·1	4·11 }	
	343·3	100·00	100·00

A portion of a brownish red compound of azoerythrine with oxide of lead, prepared by mixing a solution of azoerythrine in potash water, rendered very nearly exactly neutral by acetic acid, with a solution of tribasic acetate of lead, was analysed as follows, having been previously dried at a temperature of 180°.

0·657 gramme gave 0·456 of carbonic acid, and 0·177 of water.

0·746 gramme gave 0·112 of metallic lead, and 0·251 of oxide of lead.

These results are expressed by the formula $C_{22}\,H_{19}\,N\,O_{22} + 3\,Pb\,O$, by which is obtained

		Theory.		Experiment.
22 Carbon . .	=	134·2	19·79	19·33
19 Hydrogen .	=	19·0	2·80	3·00
22 Oxygen . .	=	176·0 }	28·03	27·88
1 Nitrogen . .	=	14·1 }		
3 Oxide of lead	=	334·8	49·38	49·79
		678·1	100·00	100·00

These numbers are confirmatory of the constitution of the substance as analysed when uncombined, and hence the formula given above may be looked upon as well established, although the number of analyses was limited to those above given, from the very small quantity of the substance which I obtained in a sufficiently pure condition. The connexion of this formula with that of the erythrine series is at once seen from the permanence of the twenty-two atoms of carbon which characterize that group of bodies, among which the erythryline appears to be that from which the azoerythrine is most directly and simply formed, in fact

One equivalent of erythryline	$C_{22}\,H_{16}\,O_{6}$
One equivalent of ammonia	$H_{3}\quad N$
Sixteen equivalents of oxygen	O_{16}
One equivalent of azoerythrine	$C_{22}\,H_{19}\,O_{22}\,N.$

To explain the formation of azoerythrine from amarythrine, which is the highest member of the erythrine series by which we can consider it to be produced, we must suppose three equivalents of water to become fixed in the substance, thus:

One equivalent of amarythrine	$C_{22}\,H_{13}\,O_{14}$
One equivalent of ammonia	$H_{3}\quad N$
Three equivalents of water	$H_{3}\,O_{3}$
Five equivalents of oxygen	O_{5}
One equivalent of azoerythrine	$C_{22}\,H_{19}\,O_{22}\,N.$

The fixation of these three equivalents of water in a form not capable of being separated by combination with oxide of lead, appears to me not very likely, but if they could be eliminated, and that the formula of dry azoerythrine became $C_{22}\,H_{16}\,O_{19}\,N$, a difficulty in the theory of the production of orceine would be removed, the nature of which will hereafter be pointed out. It is possible that the analysis of a more basic salt of lead, or of a salt of silver, might demonstrate that these three equivalents of water may be replaced, or that even by a higher temperature they might be removed.

II. *Of Orceine.*

This substance, as prepared by the process already described, is of a fine red colour, very sparingly soluble in water, which however it colours a very beautiful pink, and from which it is precipitated totally on the addition of any soluble neutral salt. It is copiously soluble in alcohol, the solution being of a splendid crimson colour, and being precipitated by the addition of water. It is but very sparingly soluble in ether. Orceine dissolves easily in a watery solution of potash or of ammonia, giving a magnificent purple liquor, the colour of ordinary archil, from which the colouring matter may be totally removed by the addition of an excess of common salt. An alkaline orceinate gives with metallic salts, lakes of very beautiful purple of various shades, which however lose a great deal of their lustre on being dried.

On commencing the analysis of this substance, I was met by a degree of discord-

ance and irregularity in my results, which at once showed me that specimens obtained at different times from different portions of archil had totally different elementary constitutions. I soon found, however, that this difference fell altogether upon one constituent, the oxygen, for it appeared that the carbon, hydrogen, and nitrogen were always in the same proportion to each other, but that the amount of oxygen present in the substance was liable to variation. At length, after a numerous series of analyses, I was enabled to assign the limits within which the variations were included, and to satisfy myself that the orceine, as prepared from archil, is in most cases a mixture of two substances, the proportions of which vary with the age of the archil, the oldest archil containing the most highly oxidized orceine.

These are the substances, the existence of which I indicated under the head of archil, and to which I propose to give the names of Alphaorceine and Betaorceine. In all essential chemical properties they are identical. The same degrees of solubility in water, in alcohol, and in ether; generating the same purple liquor with the alkalies, and the same purple coloured lakes with metallic oxides; and in all cases to be distinguished from each other by the results of their ultimate analysis alone.

Under such circumstances it would be useless to bring forward the numerous analyses which I made of specimens, which were ultimately shown to have been mixtures of the two varieties. On this account I shall only bring forward those experiments by which I was enabled to assign the greatest and least quantities of oxygen which orceine is liable to contain, and which were given by specimens obtained from portions of archil differing very much in age.

For the determination of the azote, however, although variable mixtures were employed, the results were always satisfactory; indeed the relation of the carbon to the nitrogen being the same in both varieties, the relative volumes of nitrogen and carbonic acid, determined by the method which I followed, was the same as if perfectly pure specimens of either were employed, and the results which follow were obtained by the combustion of ordinary mixed orceine.

Tube.	$CO_2 + N$.	N.		CO_2.		N. : CO_2.
A.	600	31·4	=	568·6	∴	1 : 18·1
B.	151	7·8	=	143·2	∴	1 : 18·3
C.	552	28·3	=	523·7	∴	1 : 18·5
D.	373	19·0	=	354·0	∴	1 : 18·6
E.	226	11·5	=	214·5	∴	1 : 18·7

These results, which agree unusually well with each other, fix the relation of carbon to azote as eighteen atoms of the former to one of the latter. This is the same proportion which Liebig assigned from considerations on the production of orceine from orcine, and hence the proportion of sixteen to one, assigned by Dumas from his analysis of orceine, was thrown rather too low. The difference in the proportion of azote per cent., on the supposition of eighteen to one, or of sixteen to one, not being quite 0·5 per cent., and hence being completely included within the limits of error unavoidable in so difficult a process.

I will now proceed to describe the analyses which were made of the two forms of orceine and of their salts.

A. *Analysis of Alphaorceine.*

A. 0·302 gramme of substance gave 0·829 of carbonic acid, and 0·192 of water.

B. 0·417 gramme gave 0·950 of carbonic acid, and 0·229 of water.

These results lead to the formula $C_{18}\ H_{10}\ N\ O_5$, giving

	Theory.		Experiment A.	Experiment B.
18 Carbon . .	109·8	63·14	63·32	63·04
10 Hydrogen .	10·0	5·75	5·89	6·11
1 Nitrogen . .	14·1	8·11	30·79	30·85
5 Oxygen . .	40·0	23·00		
	173·9	100·00	100·00	100·00

A solution of alphaorceine in ammonia was decomposed by acetate of lead, and the mixed liquors rendered exactly neutral by the cautious addition of acetic acid; there was produced a beautiful purple precipitate, which dried at 212°, gave the following results, from which the formula $C_{18}\ H_{10}\ N\ O_5 + 3\ Pb\ O$ may be deduced.

0·531 of substance gave 0·409 of carbonic acid, and 0·106 of water.

0·354 gave 0·162 of oxide of lead, and 0·067 of metallic lead.

The numerical results are hence

	Theory.		Experiment.
18 Carbon . .	109·8	21·58	21·29
10 Hydrogen .	10·0	1·97	2·21
1 Nitrogen . .	14·1	10·63	10·37
5 Oxygen . .	40·0		
3 Oxide of lead	334·8	65·82	66·13
	508·7	100·00	100·00

B. *Analysis of Betaorceine.*

The betaorceine was, previous to analysis, dried in Liebig's apparatus at a temperature of 212°.

A. 0·201 gramme of material gave 0·402 of carbonic acid, and 0·097 of water.

B. 0·248 gramme of same substance gave 0·493 of carbonic acid, and 0·113 of water.

C. 0·381 gramme of a different specimen gave 0·752 of carbonic acid, and 0·169 of water.

These results give in 100 parts

	A.	B.	C.
Carbon	55·30	54·97	54·58
Hydrogen	5·35	5·07	4·92
Oxygen and Azote .	39·35	39·96	40·50
	100·00	100·00	100·00

In the last analysis it would appear that a small quantity, 1 per cent., of the substance had been lost.

The formula deduced from these numbers being the same with that adopted for orceine by LIEBIG, $C_{18} H_{10} N O_8$ gives the result:

18 Carbon . =	109·8	55·45
10 Hydrogen. =	10·0	5·05
1 Nitrogen . =	14·1	39·50
8 Oxygen . =	64·0	
	197·9	100·00

differing from alphaorceine in containing three equivalents more of oxygen.

To determine the constitution of betaorceine in its salts, an ammoniacal solution of betaorceine was mixed with a solution of acetate of lead, and the liquor having been rendered neutral by the addition of acetic acid, the fine purple precipitate which formed was collected, and having been washed until all excess of lead had been completely removed, it was dried in a stove, the temperature of which did not exceed 150° FAHR. It still, however, contained combined water, and in order to obtain it anhydrous, it was dried in LIEBIG's apparatus at 212°, after which it did not part with any more water, although oil at 280° was used as the source of heat. 1·600 gramme dried in this way gave 1·377 of dry substance, hence it contained 13·94 per cent. of combined water. In the anhydrous state it was analysed.

A. 1·111 gramme gave 0·313 of oxide of lead, and 0·345 of metallic lead.

0·710 gramme of the same substance gave 0·526 of carbonic acid, and 0·131 of water.

B. 0.642 of another quantity prepared at a different time, and dried in an oil bath at 250° FAHR. gave 0·443 of carbonic acid, and 0·105 of water.

0·314 of the same substance gave 0·198 gramme of oxide of lead.

The formula $C_{18} H_{10} N O_8 + 3 Pb O$ expresses very accurately the results so obtained; the numbers in 100 are

	Theory.		Experiment A.	Experiment B.
18 Carbon . . =	109·8	20·62	20·49	19·35
10 Hydrogen . =	10·0	1·88	1·93	1·82
1 Nitrogen . . =	14·1	14·66	16·19	15·78
8 Oxygen . . =	64·0			
3 Oxide of lead =	334·8	62·84	61·39	63·05
	532·7	100·00	100·00	100·00

This compound, as dried, when first precipitated at 150° appears to have retained nine equivalents of water, which would give 13·2 gramme per cent.; the quantity obtained having been 13·97.

A compound of betaorceine with oxide of copper was prepared with the same precautions, which were made use of in the cases already described. It was then dried

in a stove until it ceased to lose weight. It was of a very rich purple-brown colour. Its analysis took place as follows:

1·113 gramme dried in LIEBIG's apparatus at a temperature of 212°, gave 0·997 of dry substance, indicating the presence of 10·6 water in 100 parts.

0·721 gramme of the hydrated substance, ignited until all organic matter was completely burned out, the resulting mixture of oxide and metallic copper moistened with nitric acid and again ignited, gave 0·209 gramme of oxide of copper, corresponding to 29·0 per cent. for the hydrated, and to 32·37 per cent. for the dried substance.

0·709 gramme of the dried substance gave 0·787 of carbonic acid, and 0·250 of water.

These results indicate the formula $C_{18}\ H_{14}\ N\ O_{12} + 3\ Cu\ O$ for the substance dried at 212°, giving

	Theory.		Experiment.
18 Carbon . . . =	109·8	31·14	30·68
14 Hydrogen. . . =	14·0	3·96	3·92
1 Nitrogen . . . =	14·1	31·22	33·03
12 Oxygen . . . =	96·0		
3 Oxide of copper. =	118·8	33·68	32·37
	352·7	100·00	100·00

In this form the substance contained therefore still four atoms of water, the formula being really $C_{18}\ H_{10}\ N\ O_8 + 3\ Cu\ O + 4\ H\ O$; and as dried at 150°, it appears to have contained four more, which should give 9·3 per cent., or five more, which should give 11·3 per cent. of hydrate water, the experimental result being 10·6. I consider it most likely that in the fresh precipitated form this compound is expressed by $C_{18}\ H_{10}\ N\ O_8 + 3\ Cu\ O + 9\ H\ O$.

It may, therefore, be now considered as definitely fixed that the betaorceine is identical with the orceine discovered by ROBIQUET and analysed by DUMAS; and that the formula $C_{18}\ H_{10}\ N\ O_8$, proposed by LIEBIG, truly expresses its constitution.

In the analysis of orceine DUMAS obtained 55·9 per cent. of carbon, whilst the formula he adopted, $C_{16}\ H_9\ O_7\ N$, required only 55·3. I would refer this to the presence of some alphaorceine, for indeed his results express the constitution of the mixtures of the two orceines which exist very generally in archil. In analysing mixed orceine the carbon generally falls between 56 and 57 per cent., and several times came out almost precisely what DUMAS obtained; but considering the almost constant co-existence of alphaorceine, it is certain that the lowest value obtained in good analyses is that which assigns its true proportion. It is much rarer to find the carbon approximating to the quantity contained in alphaorceine, and I met with pure alphaorceine only once out of the great number of specimens of archil I examined. DUMAS supposed his formula to be confirmed by the analysis of the silver salt, which contained 58·6 of oxide of silver, whilst theory required 58; the true formula of a bibasic salt giving the quantity of oxide of silver 54·0 per cent. I consider the differ-

ence here to have arisen from admixture of a still more basic salt, produced by the presence of a slight excess of ammonia in the solution of orceine. Indeed, by boiling the solution of orceine in ammonia, the excess of ammonia cannot be completely driven off, so as to leave any kind of neutral compound; and to form salts of definite constitution I found it indispensable to add small quantities of acid to the mixed liquors, so as to leave the supernatant liquor exactly neutral. If the acid be in excess the precipitate becomes contaminated by some orceine which separates along with it. The washing of these salts of orceine must be continued until the filtered liquors become tinged crimson, owing to a certain quantity of the orceine salt itself being dissolved, which does not happen until the removal of the foreign saline matter has been nearly perfect.

In order to ascertain the constitution of the violet compound of ammonia and of orceine, 0·273 of betaorceine was kept in a current of dry ammonia as long as any increase of weight took place. The combination was accompanied with the evolution of heat, and the violet-coloured substance which resulted was found to weigh 0·295 gramme. On exposure to a temperature of 212° in a current of air, the ammonia was after some time totally removed, and the betaorceine remained unaltered. This proportion of ammonia corresponds to 8·06, absorbed by 100 of betaorceine, very closely approximating to 8·58, which theory gives equivalent to an atom. The violet compound is therefore to be considered as $C_{18} H_{10} N O_8 + N H_3$; and I have found that the betaorceine when dried at 150° FAHR. retains an equivalent of water, which it loses at 212°, and that consequently the bodies $C_{18} H_{10} N O_8 + Ad H$ and $C_{18} H_{10} N O_8 + O H$ are equivalent to one another. This hydrate of betaorceine is of a much lighter colour than the anhydrous compound, and it will be hereafter shown that a corresponding body, $C_{18} H_{10} N O_8 + S H$, is capable of being formed.

The most important question in the philosophical history of these bodies, that of their origin, requires now to be discussed, and as there is but little doubt that the betaorceine, $C_{18} H_{10} N O_8$, is formed by the gradual oxidation of the alphaorceine, $C_{18} H_{10} N O_5$, our views need only involve the production of the latter compound. In the case of archil prepared from the *Variolaria dealbata*, where the primitive substance is orcine, the production of orceine is easily understood; the dry orcine having the constitution $C_{18} H_7 O_3$, it requires only the combination of an atom of ammonia and the absorption of two or five equivalents of oxygen to form the one or the other variety of orceine. But in the case of ordinary archil, where the *Parmelia* or the *Roccella* had been used, the transition from the erythrine series to that of orceine becomes much more complex, as not only a certain quantity of hydrogen, but also four equivalents of carbon must be removed; the substances of the former group containing twenty-two atoms of that element, while those of the latter include only eighteen.

The azoerythrine is probably the substance which forms the transition between the two groups, and from it the origin of alphaorceine can easily be explained.

An equivalent of azoerythrine is .	$C_{22}\ H_{19}\ N\ O_{22}$
It gives off four carbonic acid . .	$-C_{4}\quad -O_{8}$
And nine of water	$-H_{9}-O_{9}$
An equivalent of alphaorceine . .	$C_{18}\ H_{10}\ N\ O_{5}$

From the very small quantity of azoerythrine which I could find present in archil, at any one moment, it is probably decomposed as fast as formed, very nearly, and either orceine may be considered as arising directly from amarythrine as follows:

An equivalent of amarythrine. . .	$= C_{22}\ H_{13}\ O_{14}$
An equivalent of ammonia. . . .	$H_{3}\quad N$
Five equivalents of oxygen. . . .	O_{5}
	$C_{22}\ H_{16}\ O_{19}\ N$
Gives four equivalents carbonic acid.	$C_{4}\quad O_{8}$
Six equivalents of water.	$H_{6}\ O_{6}$
and an equivalent of alphaorceine .	$C_{18}\ H_{10}\ O_{5}\ N$
	$C_{22}\ H_{16}\ O_{19}\ N$

It is, however, most likely that the amarythrine is all changed into azoerythrine before forming orceine, and hence that azoerythrine has the formula $C_{22}\ H_{16}\ N\ O_{19}$, the three equivalents of water I found being probably in a form capable of elimination.

It is also possible that from telerythrine the betaorceine may be at once formed. Thus

An equivalent of telerythrine. . .	$= C_{22}\ H_{9}\ O_{18}$
An equivalent of ammonia . . .	$H_{3}\quad N$
	$C_{22}\ H_{12}\ O_{18}\ N$

should give

Four equivalents of carbonic acid .	$C_{4}\quad O_{8}$
Two equivalents of water	$H_{2}\ O_{2}$
An equivalent of betaorceine . . .	$C_{18}\ H_{10}\ O_{8}\ N$
	$C_{22}\ H_{12}\ O_{18}\ N$

I do not think it probable that this reaction ever occurs in the actual manufacture of archil. In contact with air and ammonia, the erythryline can scarcely advance beyond the condition of amarythrine, and from it the azoerythrine being produced by the direct combination of the ammonia, the alphaorceine is ultimately formed.

III. *Of Erythroleic Acid.*

This is the crimson substance, distinguished by its semifluid consistence at ordinary temperatures, and its solubility in ether, which is obtained by treating the solid extract of archil by warm sulphuric ether, as already described. It possesses no other property remarkably characteristic. It is almost insoluble in water, which,

however, it tinges pink: totally insoluble in oil of turpentine, but abundantly soluble in alcohol and ether. It dissolves in alkaline liquor, forming a fine purple (crimson) coloured solution, and is precipitated therefrom by an acid or a neutral salt. It forms, with metallic oxides, crimson lakes.

By careful trial it was found that the erythroleic acid contains no nitrogen.

0·318 gramme gave on analysis 0·744 gramme of carbonic acid, and 0·267 of water.

The formula $C_{26}\ H_{22}\ O_8$ is thereby indicated, giving

	Theory.		Experiment.
26 Carbon . .	158·6	64·84	64·70
22 Hydrogen .	22·0	9·00	9·33
8 Oxygen . .	64·0	26·16	25·97
	244·6	100·00	100·00

A quantity of a very fine crimson-purple coloured compound of this substance with oxide of lead was prepared with the remaining quantity which I possessed of this substance, and having been dried in LIEBIG's apparatus with an oil bath at 250°, it was analysed.

0·578 gramme of material gave 0·913 of carbonic acid, and 0·325 of water.

0·255 gramme of material gave 0·061 of metallic lead, and 0·015 of oxide of lead.

The resulting formula is $C_{26}\ H_{22}\ O_8 + Pb\ O$, giving

	Theory.		Experiment.
26 Carbon . . .	158·6	44·53	43·41
22 Hydrogen . .	22·0	6·18	6·24
8 Oxygen . . .	64·0	17·96	18·71
1 Oxide of lead .	111·6	31·33	31·64
	356·2	100·00	100·00

Besides the analysis of erythroleic acid, above detailed, I examined a great number of specimens which gave results, variable in the per cent. proportions, but indicating the constant relation between the carbon and hydrogen of twenty-six atoms to twenty-two atoms, whilst the source of the variations lay in the proportion of oxygen not being constant. The per cent. proportion of carbon was generally higher, and that of oxygen as much lower than the numbers given by the analysis which has been brought forward, which indeed I selected as showing the maximum of oxygen, which I found this crimson substance soluble in ether to contain. This inconstancy in the constitution of erythroleic acid, arises from the occasional presence of another substance, also crimson, semifluid, and soluble in ether, which I term erythroleine, and which I shall describe in detail hereafter. These two bodies are related to each other nearly as the two orceines, and like them are distinguishable only by analysis.

In order to trace the origin of this remarkable substance, which from the minute quantity in which it exists is evidently a collateral product, it is necessary to recur to

the examination of the archil weed. Besides the erythryline, which is the origin and basis of the archil series, I noticed the existence in small quantity of the roccellic acid of HEEREN, which, however, I found in so small quantity that I could not institute any analyses of it or of its compounds. It was looked upon by HEEREN as being distinct from the bodies which produce colour, and so far as the proper orceine (lichen-red) is concerned, with perfect justice, but when we consider its constitution there can be little doubt of its being the source of erythroleic acid. We possess an analysis of it by LIEBIG, made with a portion sent to him by HEEREN, and certainly the highest confidence may be reposed in his result. The formula $C_{16} H_{16} O_4$ was adopted by LIEBIG, and his numbers are

	Theory.	Experiment.
Carbon . . .	67·05	67·94
Hydrogen . .	10·95	10·76
Oxygen . . .	22·00	21·30
	100·00	100·00

LIEBIG remarks that the formula $C_{17} H_{17} O_4$ agrees still better with his results, but he prefers the simpler 4 ($C_4 H_4 O$). A formula, however, which requires less carbon and more hydrogen than was obtained in the analysis of a pure substance cannot be adopted, and this objection applies to $C_{17} H_{17} O_4$ also, though not in so great a degree. The only support indeed which this formula receives is from an experiment made by HEEREN, who found that the roccellate of lime contained 15·9 of lime per cent., the oxygen of which is one fourth that of the roccellic acid. On this isolated result I do not consider that much stress can be laid; and as this roccellic acid, or as I propose to term it, roccelline, is the only constituent of lichen possessing hydrogen enough to allow of the formation of erythroleic acid, I would suggest to chemists the probability of its formula being rather $C_{26} H_{24} O_6$, from which are obtained the numbers.

	Theory.		Experiment.
26 Carbon . =	158·6	68·78	67·94
24 Hydrogen	24·0	10·40	10·76
6 Oxygen .	48·0	20·82	21·30
	230·6	100·00	100·00

A sesquisalt of this acid ($C_{26} H_{24} O_6$) + $\frac{3}{2}$ Ca O should give 15·6 of lime, and was perhaps that analysed by HEEREN.

The proposed formula being assumed, it is very easy to show how from it erythroleic acid may be formed.

$$\begin{array}{lr} \text{An equivalent of roccelline . . . . } = & C_{26}\, H_{24} \quad O_6 \\ & - H_2 + O_2 \\ \hline \text{An equivalent of erythroleic acid . . . . } = & C_{26}\, H_{22} \quad O_8 \end{array}$$

The characteristic constituents of archil, viz.

1. Azoerythrine.
2. Alphaorceine.
3. Betaorceine.
4. Erythroleic acid.

having been now described, and the decompositions by which they originated having been reduced to laws, I shall proceed to the next portion of my subject, the constitution of ordinary litmus.

Section III. *Of Litmus.*

In order to obtain in an isolated form the constituents of litmus, the following method was had recourse to.

The cubical masses of commercial litmus having been reduced to a fine powder, are first treated with boiling water as long as the solution comes away much coloured. The mass of insoluble matter which remains, and which is of a paler blue than the original substance, is to be then diffused through water so as to form a thin cream, and muriatic acid added until all effervescence has ceased, and the thick opaque brick-red liquor reacts very acid. The whole is to be thrown upon a filter, and the red substance which remains is to be washed with water until all excess of muriatic acid has been removed, and is then to be carefully desiccated.

When completely dry, this mass is to be boiled in successive portions of alcohol, until every thing soluble in that fluid shall have been taken up. The deep red alcoholic liquors are to be then distilled in a water-bath to dryness, and the resulting solid material digested in warm sulphuric ether until it no longer becomes coloured. The ethereal solutions thus obtained, yield on distillation in a water-bath a fine crimson oily material, which is nearly fluid. To obtain this free from some of the other substances which the larger quantity of ether might have taken up, it may be redissolved in a small quantity of ether, and the solution after standing for some hours, decanted from any trace of insoluble matter, and evaporated to expel all the ether, for which purpose exposure for some time to a temperature above 212° is requisite. To the substance thus obtained I give the name of Erythrolein.

The substance from which the erythrolein has thus been removed, and which is distinguished by its solubility in alcohol, must be dried in a current of air at a temperature of 212° to expel all residual traces of ether, and may then be considered pure. To it I give the name of Erythrolitmine.

The brownish red mass which resisted the action of the alcohol, yields its colouring material but very sparingly to water also. To obtain it in an isolated form, one or other of two plans may be followed. 1st, The reddish brown mass may be boiled in large quantities of pure water, which becomes coloured pretty deeply, and by evaporating these reunited liquors, a deep blood-red mass is obtained, consisting of pure colour-

ing material; or 2nd, the reddish brown mass may be boiled in water of ammonia, in which it dissolves, giving a blue solution. When this is evaporated to dryness, the greater part of the ammonia separates, and to remove the last traces, the residual mass may be moistened with dilute muriatic acid, and then washed with alcohol until the excess of acid and the sal-ammoniac have been removed. To this substance I give the name of Azolitmine.

The blue liquors which are obtained in the first place, by digesting the litmus cakes in boiling water, contain but a very small quantity of colouring matter, in comparison to what might be expected from the great depth of colour they present. To obtain this colouring matter in a pure condition, a solution of acetate of lead is to be added, and the purple precipitate which falls, having been well washed, is to be treated while still moist with a current of sulphuretted hydrogen, until completely decomposed. The resulting compound of the colouring matter with the sulphuret of lead is to be very well washed to remove all excess of sulphuretted hydrogen, and then digested in warm water of ammonia: a deep blue liquor is obtained, which is to be evaporated to dryness, and then moistened with muriatic acid and washed with warm alcohol to remove the sal-ammoniac which is formed. The colouring material remains as a deep brown-red powder.

In most cases this substance will be found to be azolitmine nearly pure, but I have met it totally free from azote, and to constitute a peculiar substance, resembling azolitmine in properties, but remarkably distinct from it in constitution. This substance is very rare in litmus. It constitutes but a very unimportant portion of the colouring substance, and hence I propose, for the adoption of chemists, the name Spaniolitmine, to distinguish it from the constant constituents already noticed, the Greek word σπανιος signifying rare.

The colouring constituents of litmus are therefore in their natural condition red, and the blue of litmus is produced by combination with a base. There are, properly speaking, only two characteristic colouring matters in litmus, the erythrolitmine and the azolitmine. For the erythrolein is coloured crimson purple only by alkalies, and the spaniolitmine occurs but very seldom. In the litmus of commerce these colouring substances are combined with lime, potash, and ammonia, and there is mixed up in the mass a considerable quantity of chalk and sand.

I shall now proceed to the detailed account of the constitution and properties of these various substances.

I. *Of Erythrolein.*

This substance, as obtained by evaporating the ethereal solutions, is semifluid at ordinary temperature, and completely liquid at 100° Fahr. Its solution in ether is of a very fine red colour. It dissolves in alcohol with the same colour, and tinges water pink, without however dissolving in any very sensible proportion. It is insoluble in oil of turpentine, and dissolves in water of ammonia, with a magnificent

purple colour, without any trace of blue. It is not volatile, and yields, when heated strongly, the usual products of decomposition of substances which contain no azote, from which substance its analysis shows it to be completely free. With metallic salts it generates fine purple lakes by double decomposition. It will be at once seen that in all these properties it identifies itself with the substance detected in archil termed erythroleic acid; it is, however, more easily fusible, and, as will be now seen, differs in constitution.

The analysis of many specimens of this substance, prepared at different times, and with different parcels of litmus, furnished results somewhat discordant as to the quantity of oxygen, which they indicated this substance to contain, but giving constantly the same relation between the carbon and the hydrogen, as has been already shown to exist in the erythroleic acid; and I ultimately met with a quantity of this substance, which I consider to have been pure, and which although small, yet gave a result so definite and characteristic, that I shall detail it as expressing the true constitution of this remarkable body. It furnished the largest amount of carbon I obtained in any instance.

0·283 gramme of material gave 0·760 of carbonic acid, and 0·272 of water.

These numbers indicate the formula $C_{26} H_{22} O_4$, by which the results are as follows:

	Theory.		Experiment.
26 Carbon .	158·6	74·43	74·27
22 Hydrogen	22·0	10·33	10·68
4 Oxygen .	32·0	15·24	15·05
	212·6	100·00	100·00

In order to test this formula by the analysis of the compound of erythrolein with oxide of lead, I prepared a portion of it by precipitating the solution of erythrolein in ammonia, by means of a solution of acetate of lead. The fine purple lake which was produced was dried at 212° in LIEBIG's apparatus, and then analysed. The result did not give any simple relation between the oxide of lead and the equivalent of erythrolein, owing probably to the accidental omission of the precautions I have already noticed as being necessary in preparing salts of this kind, but the organic matter had exactly the same composition as was given in the first experiment; there did not appear to have been any replacement of water.

The formula of erythroleic acid being $C_{26} H_{22} O_8$, it will be at once seen that the erythrolein contains half as much oxygen to the same hydrogen and carbon. Indeed, I consider the fluctuations in the results of my analyses of erythrolein and erythroleic acid, which for a long time gave me great trouble and embarrassment, to be caused by their simultaneous presence as products of the same chain of reaction. In archil the erythroleic acid appears to preponderate, as the mixed erythrolein from archil seldom gives above 67 per cent. of carbon, whilst in litmus the erythrolein, when analysed, seldom gives a value for carbon below 70 per cent., and generally 72

or 73. The total quantity of these substances is, however, very small, and it is necessary to operate upon at least a pound of commercial litmus to obtain twelve or fifteen grains of erythrolein.

Regarding the origin of this substance, I shall make no remark until the substance next in order has been described.

II. *Of Erythrolitmine.*

This substance, which from its composition and the quantity in which it exists, constitutes one of the most important ingredients in litmus, is to be obtained in the manner described under the head of the general analysis of litmus. By exposure to a temperature of 230° FAHR. for an hour or two, it may be completely freed from all chance of contamination by adhering ether.

It is of a beautiful and pure bright red colour, without any tinge of crimson. It is sparingly soluble in water, which it colours red: very sparingly soluble also in ether, which it scarcely tinges, but abundantly soluble in alcohol, forming a fine deep red liquor, which if saturated when boiling, deposits on cooling a considerable quantity of erythrolitmine under the form of small soft granular crystals, which are not at all brilliant, though of a fine deep red colour. This is the only colouring substance in all this series, in which I have been able to detect the slightest disposition to crystallize.

In a pretty strong solution of potash the erythrolitmine dissolves, giving a blue liquor. With ammonia it combines, forming a blue substance, which has the singular character of being totally insoluble in water. Although the erythrolitmine is itself very sparingly soluble in water, yet if water tinged by means of it be mixed with some water of ammonia, the blue compound gradually subsides, or may be removed by filtration, leaving the liquor absolutely colourless. The separation of this erythrolitmine-ammonia may be accelerated by boiling. This blue compound is, however, very instable; it cannot be dried without losing ammonia and becoming reddish purple. In this state it still retains a portion of the ammonia very firmly, so that it cannot be separated by means of heat. The erythrolitmine combines with metallic oxides, and forms lakes of a very fine purple colour; their preparation, however, requires precautions, to which I shall hereafter direct attention.

The erythrolitmine dried at 212°, gave on analysis the following results, with separate specimens.

A. 0·422 gramme of material gave 0·853 of carbonic acid, and 0·330 of water.

B. 0·423 gramme of material dried at 250°, gave 0·844 of carbonic acid, and 0·311 of water. The composition indicated by these results is

	Theory.		A.	B.
26 Carbon	= 158·6	55·53	55·78	55·3
23 Hydrogen	= 23·0	8·05	8·69	8·1
13 Oxygen	= 104·0	36·42	35·43	36·6
	285·6	100·00	100·00	100·0

The second quantity of substance was dried at 250° in order to determine whether the twenty-third atom of hydrogen arose from accidentally-present water. It is evident, consequently, that the true formula of the erythrolitmine is $C_{26} H_{22} O_{12} + Aq$. When the substance has been dried below 212°, it retains, though loosely, another equivalent of water, which corresponds to almost exactly three per cent. It is then $C_{26} H_{22} O_{12} + 2 Aq$.

If dry ammonia be passed over erythrolitmine, it is absorbed with the production of considerable heat, and if the substance containing 2 Aq be employed, the second equivalent of water is expelled. The resulting mass is deep blue. When this mass is heated to 212°, it loses the blue colour and a portion of ammonia is expelled, a dark reddish purple mass remaining, from which, however, all ammonia cannot be expelled. The action is therefore the same with the dry gas as with ammonia dissolved in water.

This description is substantiated by the following experiments.

0·709 of the bihydrated substance, $C_{26} H_{24} O_{14}$, was exposed to a stream of dry ammonia until all the water, which at first separated, had been removed by the excess of gas, and the substance had become quite dry and cold. It then weighed 0·729. It was then heated in a current of air to 250° FAHR. until it ceased to lose weight, when it weighed 0·687 gramme. Theory indicates the following result.

$$\begin{array}{rcr} C_{26} H_{22} O_{12} & = & 276·6 \\ 2 H O & = & 18·0 \\ \hline & & 294·6 \end{array} \qquad \begin{array}{rcr} \text{Substance} & = & 276·6 \\ \text{give } H O & = & 9·0 \\ N H_3 & = & 17·1 \\ \hline & & 302·7 \end{array} \qquad \begin{array}{rcr} \text{Substance} & = & 276·6 \\ \text{and then } \frac{N H_3}{2} & = & 8·5 \\ \hline & & 285·1 \end{array}$$

$$\begin{array}{lrcrcrcr} \text{Now} & 709 & : & 729 & :: & 294·6 & : & 302·8 \\ \text{and} & 709 & : & 687 & :: & 294·6 & : & 285·5 \end{array}$$

If the erythrolitmine had given off all ammonia but retained an equivalent of water, the numerical result would have been the same, but the properties of the purple-brown substance show that it is a definite compound. It is quite insoluble in spirit, and when treated by a dilute acid, immediately assumes the bright red colour of pure erythrolitmine. In order further to test its constitution it was analysed.

0·347 gramme of substance gave 0·691 of carbonic acid, and 0·265 of water.

Hence the formula $C_{26} H_{22} O_{12} + \frac{N H_3}{2}$, which gives

		Theory.		Experiment.
26 Carbon	=	158·6	55·63	55·07
23·5 Hydrogen	=	23·5	8·24	8·48
12 Oxygen	=	96·0	36·13	36·45
½ Nitrogen	=	7·0		
		285·1	100·00	100·00

The erythrolitmine-ammonia being insoluble, the compounds of erythrolitmine with metallic oxides cannot be formed by the method of double decomposition used in so many other cases. The mode I found most convenient, was to boil the erythrolitmine with some alcohol, so as to have it partly dissolved and partly diffused in minute division through the liquor, and then to add it to a solution of basic acetate of lead. A deep purple precipitate forms, which is to be boiled for a few minutes, then well washed and filtered. Having been dried at 212° in LIEBIG's apparatus, it was analysed.

0·532 gramme gave 0·606 of carbonic acid, and 0·229 of water.

0·583 gave 0·146 of oxide of lead, and 0·105 of metallic lead.

The composition resulting from these numbers indicates the formula $C_{26}\ H_{22}\ O_{12} + 2\ Pb\ O$, which gives

	Theory.		Experiment.
26 Carbon . .	158·6	31·73	31·52
22 Hydrogen .	22·0	4·40	4·78
12 Oxygen . .	96·0	19·21	19·27
Oxide of lead	223·2	44·66	44·43
	499·8	100·00	100·00

The twenty-third equivalent of hydrogen is here eliminated and replaced by oxide of lead, the true formula of the erythrolitmine is therefore $C_{26}\ H_{22}\ O_{12}$.

It is evident that this substance belongs to the same series of bodies as the erythrolein and the erythroleic acid, the relation of the carbon and hydrogen being the same, the oxygen, however, having increased to twelve equivalents. That this body is a direct product of the oxidation of erythroleic acid, is completely shown by the fact, that if semifluid erythroleic acid be left exposed to the air for some weeks, it gradually solidifies; it is then insoluble in ether, is coloured blue by ammonia, and is, in fact, found to have been changed into erythrolitmine. The bodies are therefore related to each other as the two orceines.

The origin of erythrolein is a point on which, however, I do not at all feel perfectly decided. It will be recollected how beautifully simple the production of erythroleic acid from roccelline appeared to be, two equivalents of hydrogen being replaced by two of oxygen. The production of erythrolein does not appear to me by any means so easily explained. The relation between roccelline and erythrolein is extremely simple.

$$\underset{\text{Roccelline.}}{C_{26}\ H_{24}\ O_6} = \underset{\text{Erythrolein.}}{C_{26}\ H_{22}\ O_4} + 2\ H\ O.$$

And if we looked no further, it might easily be said that by a metameric change the roccelline, in decomposing, yielded erythrolein and water, and that afterwards the absorption of oxygen gave from

$$\begin{aligned} \text{Erythrolein} &= C_{26}\ H_{22}\ O_4, \\ \text{Erythroleic acid} &= C_{26}\ H_{22}\ O_8 \text{ and} \\ \text{Erythrolitmine} &= C_{26}\ H_{22}\ O_{12}, \end{aligned}$$

a chain of reactions among the simplest possible.

If this were so, we should, however, find erythrolein existing principally among the earliest products of the general breaking up of the colourless substances in the lichen, and erythroleic acid should co-exist in quantity with erythrolitmine among the latter results of gradual oxidation. This, however, is not the case. In archil, the earliest stage, there is but a mere trace of erythrolein and of erythrolitmine, but abundance (comparatively speaking) of erythroleic acid, whilst in the litmus, where the train of decompositions is much more advanced, scarcely a trace of erythroleic acid can be found, but the erythrolein makes its appearance in greater quantity, and a great portion of the colouring matter of the litmus is erythrolitmine. I am hence induced to consider these substances as formed in the following order. By the reaction already described, the roccelline is converted into erythroleic acid, which then breaks up into erythrolein and erythrolitmine, as it can be seen that

$$\underset{\text{Two atoms erythroleic acid.}}{C_{52}\,H_{44}\,O_{16}} = \underset{\text{One erythrolein.}}{C_{26}\,H_{22}\,O_{4}} + \underset{\text{Erythrolitmine.}}{C_{26}\,H_{22}\,O_{12}}$$

The erythrolein, I consider, may then absorb oxygen and form erythroleic acid, which will be again broken up and ultimately all converted into the final term erythrolitmine. In the commencement, therefore, the erythroleic acid is tolerably permanent until the roccelline is all exhausted; and indeed its permanency is promoted by the fact that in making archil too rapid an oxidation might do much harm, the alphaorceine being a richer colour than the betaorceine. But in making litmus it is decomposed, and whilst the great mass rapidly forms erythrolitmine, small quantities of erythrolein appear to escape the action of the air.

Finally, to sum up the results of this part of the investigation, I look upon these three bodies as all derived from roccelline; but notwithstanding the beautiful simplicity of their formulæ, which would appear to indicate them to be all oxides of one compound radical, which contained $C_{26}\,H_{22}$, I look upon them as, when once formed, being quite independant of each other: thus, if erythrolitmine was erythrolein + eight oxygen, we should be able, by deoxidizing means, to change erythrolitmine into erythrolein; this cannot be done, and hence, as will be shown more fully when describing the results of decolorization of these bodies, I look upon each as having an internal constitution distinct from either of the others.

III. *Of Azolitmine.*

The preparation of the azolitmine has been already described: it constitutes almost pure, the substance separated by means of muriatic acid, and insoluble in alcohol. It is sparingly soluble in water, and still more soluble in water of potash or of ammonia, with which it forms the peculiar blue of litmus, and may be obtained, as already noticed, either by evaporating the aqueous solution, or by treating the ammonia compound with a little muriatic acid and warm alcohol.

As thus prepared the azolitmine is a deep brownish-red powder, totally destitute of crystalline texture. Its general characters of solubility, &c. are indicated by the

mode by which it is prepared, and it is distinguished by being coloured pure blue by the alkalies, and by containing nitrogen as a constituent.

Its analysis was effected as follows: the determination of the azote was effected by the same method of relative volumes of the carbonic acid and nitrogen gases employed in the other instances. The best precautions were taken to ensure success, and the results, though not so uniform as in other instances, owing probably to some irregularity in the combustion, gave a proportion almost exactly eighteen carbon to one of azote. The detail of numbers follows:

No. of Tube.	$CO_2 + N$.	N.	CO_2.		N : CO_2.
A.	128	7	121	∴	1 : 17·3
B.	318	17	301	∴	1 : 18·3
C.	196	11	185	∴	1 : 16·8
D.	528	28	500	∴	1 : 17·8

The mean result is 1 : 17·6, nearly 1 : 18, which number I therefore adopt. The relation of carbon to azote is thus the same as in orceine.

A. 0·307 of substance dried at 212° gave 0·550 of carbonic acid, and 0·148 of water.

B. 0·376 gramme of another quantity, dried also at 212°, gave 0·683 carbonic acid, and 0·187 of water. Hence in 100 parts

	A.	B.
Carbon	49·50	50·05
Hydrogen	5·35	5·52
Oxygen and azote . .	45·15	44·43
	100·00	100·00

The carbon being to the azote as 18 : 1. there are two formulæ which express nearly the results of the analyses just described, though the accordance is not satisfactory with either formula. These formulæ are $C_{18}\, H_{11}\, O_{11}\, N$, and $C_{18}\, H_{10}\, O_{10}\, N$, giving

18 Carbon .	109·8	49·3
11 Hydrogen	11·0	4·9
11 Oxygen .	88·0	45·8
1 Nitrogen .	14·1	
	222·9	100·0

18 Carbon .	109·8	51·3
10 Hydrogen	10·0	4·7
10 Oxygen .	80·0	44·0
1 Azote . .	14·1	
	213·9	100·0

Considering the deviation of the analytical result from the numbers assigned by either formula to have arisen from imperfect desiccation, I had another portion dried carefully at 230° until no more traces of water were given off, and then it was analysed.

0·432 gramme gave 0·783 of carbonic acid, and 0·200 of water. Hence per cent.

Carbon	49·94	100·00
Hydrogen	5·14	
Oxygen and nitrogen . .	44·92	

almost identical with the former results, and indicating either the formula to be $C_{36} H_{21} N_2 O_{21}$, or that this substance retains half an equivalent of water very powerfully, and the formula becomes $C_{18} H_{10} N O_{10} + \frac{1}{2} Aq$, by which the numbers are given:

18 Carbon	50·27	100·00	109·8	218·4
10·5 Hydrogen	4·81		10·5	
10·5 Oxygen and nitrogen . . .	44·92		98·1	

I was anxious to examine the compound of this body with ammonia, but found that it gave results much less definite than those obtained with the erythrolitmine and the orceine. If the blue ammoniacal liquor be evaporated to dryness, the ammonia is expelled for the most part along with the last portion of water, but the quantity which remains behind is not constant. The absorption of dry ammonia was found also to be too irregular to be made the basis of numerical results.

The ammoniacal solution of azolitmine gives with metallic solutions precipitates which are either purple or blue, according to the proportion of metallic oxide which they contain. Using the precautions already so often described, the combinations of azolitmine with metallic oxides are produced, containing the smallest possible proportion of base, and of a fine purple. In this way the specimens were prepared, the analyses of which will now be detailed.

The *azolitmate of lead*, although of a beautiful purple when freshly prepared, loses that tint when dried with LIEBIG's apparatus in an oil bath, and becomes blue. Of a specimen dried at 250° FAHR. 1·226 gramme gave 0·512 of oxide of lead, and 0·218 of metallic lead.

1·188 gramme of the same substance gave 0·832 of carbonic acid, and 0·220 of water.

From this results the formula $C_{18} H_{10} N O_{10} + 3 Pb O$, giving

		Theory.		Experiment.
18 Carbon	=	109·8	20·01	19·35
10 Hydrogen	=	10·0	1·82	2·00
1 Nitrogen	=	14·1	17·15	19·27
10 Oxygen	=	80·0		
3 Oxide of lead . . .	=	334·8	61·02	59·38
		548·7	100·00	100·00

The salt or lake formed with protoxide of tin in the cold is of a beautiful purple colour. It gave the following result.

0·611 gramme of material gave 0·466 of carbonic acid, and 0·156 of water.

1·328 of material gave, by ignition until all organic matter was burned out, then moistening with nitric acid and subsequent ignition a second time, 0·777 of oxide of tin (peroxide) quite white.

The formula $C_{18} H_{10} N O_{10} + 4 Sn O + 2 Aq$, gives

	Theory.		Experiment.
18 Carbon . . .	109·8	22·01	21·10
12 Hydrogen . .	12·0	2·41	2·84
1 Nitrogen . . .	14·1	28·48	30·07
16 Oxygen . . .	128·0		
4 Tin.	235·6	47·10	45·99
	499·5	100·00	100·00

If a temperature be applied to this salt sufficiently high to expel the water, it becomes partly decomposed, and was hence analysed only in this hydrated condition. If when in this state it is boiled with water it becomes completely decolorized, and the tin is changed into the form of peroxide, a grayish white compound is produced, which rapidly absorbs oxygen, and generates, thereby, a red compound of regenerated azolitmine with peroxide of tin. The exact nature of the reaction to which this effect is due, will be examined in detail hereafter.

This azolitmine, which is the only constituent of litmus containing azote, appears by the analytical results just given to be connected in a most simple and remarkable manner with the principles of archil, alphaorceine and betaorceine. In fact, the proportion of carbon, of hydrogen, and of azote being the same in these bodies, they differ only in the quantity of oxygen they contain, their formulæ being

Alphaorceine . . . $C_{18} H_{10} N O_5$.
Betaorceine . . . . $C_{18} H_{10} N O_8$.
Azolitmine . . . . $C_{18} H_{10} N O_{10}$.

As in this portion of the paper I wish to confine myself to experimental results, I shall not enter now into any consideration of their theoretical nature, further than to notice, that as in the series of erythrolein and erythrolitmine, although these bodies are simply produced by the continued action of oxygen, yet when once formed they cannot be looked upon as oxides of the same compound radical, but are substances totally independent of each other.

IV. *Of Spaniolitmine.*

In the majority of cases, the salt of lead prepared from the solution of litmus in water contains only azolitmine, but in some, I recognized the presence of the substance noticed under the name of spaniolitmine in the description of the analysis of litmus, and which is distinguished from azolitmine by not containing nitrogen. The existence of this substance rendered useless a great mass of results which I had obtained in the commencement of my investigations; the substances employed having been mixtures in variable proportions of the two bodies, and having consequently given analytical expressions for the soluble colouring matter of litmus, different in each experiment. The source of this was at last traced to the presence of spaniolitmine, which, when once mixed with azolitmine, cannot be separated from it by any method

that I know of, and consequently it is not until all the labour of preparation and analysis has been gone through, that any opinion can be formed as to which substance, or what mixture of the two substances, was present. The simplest analytical means consist in collecting the mixed gases produced by the combustion of the specimen, and determining the relation by volume between the carbonic acid and the azote: if it be 18 : 1, the substance is pure azolitmine; if there be no azote, it is pure spaniolitmine, which occurs but very seldom; and, if, as is generally the case, the proportion is thirty, forty, or fifty to one, the substance is a mixture on which it is useless further to experiment. So rare is the presence of this body in a form, even nearly pure, that out of more than forty trials I obtained it in a state to justify its being made the object of quantitative investigation only twice. In one of these the absence of azote was complete, in the other a small quantity of azote remained, being 1 to 200 of carbonic acid, a proportion so small that it could not interfere with the analytical results.

The spaniolitmine resembles azolitmine and erythrolitmine, in being turned blue by alkalies. It is of a bright red colour, insoluble in alcohol and in ether, and very sparingly soluble in water, which it tinges bright red. In this respect it differs somewhat from the azolitmine, which is more soluble in water, and colours the water a darker and browner red. Its compound with ammonia is decomposed by a very moderate heat, although imperfectly, like the other bodies already noticed. Its precipitates with metallic solutions are identical in appearance with those formed by the azolitmine.

The analysis of this substanee was as follows:

0·311 gramme of spaniolitmine dried in LIEBIG's apparatus with an oil bath at 250° FAHR., gave 0·501 of carbonic acid, and 0·087 of water.

Hence results the formula $C_{18}\ H_7\ O_{16}$, giving

	Theory.		Experiment.
18 Carbon . . =	109·8	44·85	44·54
7 Hydrogen . =	7·0	2·86	3·11
16 Oxygen . . =	128·0	52·29	52·35
	244·8	100·00	100·00

A very fine purple lead salt, which had been dried at 250°, gave the following results:

From 2·648 of material were obtained 1·226 of carbonic acid, and 0·261 of water.

1·261 of material gave 0·158 of oxide of lead, and 0·661 of metallic lead.

The formula $C_{18}\ H_7\ O_{16} + 5\ Pb\,O$ gives

	Theory.		Experiment.
18 Carbon . . .	109·8	13·69	12·81
7 Hydrogen . .	7·0	0·75	1·09
16 Oxygen . . .	128·0	15·97	16·10
5 Oxide of lead .	558·0	69·59	70·00
	802·8	100·00	100·00

When this salt is dried at 180° it retains about 3·5 per cent. of water, which it loses at 250°. In this hydrated form, its constitution is probably $C_{18} H_7 O_{16} + 5 Pb O + 3 Aq$.

With oxide of silver the spaniolitmine gives a fine purple lake, which gradually becomes black on exposure to light. It was analysed.

0·894 of a portion dried at 212°, gave by ignition 0·482 of metallic silver.

1·762 gramme of the same specimen gave 1·206 of carbonic acid, and 0·271 of water.

These numbers give the formula $C_{18} H_7 O_{16} + 3 Aq O$.

	Theory		Experiment.
18 Carbon . . =	109·8	18·53	18·92
7 Hydrogen .	7·0	1·18	1·61
19 Oxygen . .	152·0	25·64	25·55
3 Silver . .	324·0	54·65	53·92
	592·8	100·00	100·00

If the solution of spaniolitmine in water of ammonia be decomposed by basic acetate of lead, there is produced a fine azure-blue precipitate, which is not altered by an excess of ammonia; and as it appeared to contain almost exactly the same quantity of oxide of lead, in portions prepared at different times, it was looked upon as being definite in constitution, and was analysed.

A. 1·762 gramme of substance dried at 250° in an oil bath, gave 0·520 of oxide of lead, and 0·900 of metallic lead, being 85·35 Pb O in 100.

B. 2·161 gramme of another portion, dried also at 250° in an oil bath with Liebig's apparatus, gave 1·159 of metallic lead, and 0·558 of oxide of lead, equivalent to 84·31 Pb O in 100.

C. 3·558 gramme of the same specimen gave 0·152 of water, and 0·846 of carbonic acid.

The formula which results is $C_{18} H_7 O_{16} + 12 Pb O$.

	Theory.		Experiment.
18 Carbon . . .	109·8	6·93	6·58
7 Hydrogen . .	7·0	0·44	0·43
16 Oxygen . . .	128·0	8·08	8·68
12 Oxide of lead .	1339·2	84·55	84·31
	1584·0	100·00	100·00

If this substance be dried at the temperature of 150° it retains five per cent. of water, which it loses completely between 212° and 250°. This quantity is almost exactly nine equivalents, and hence probably the hydrated salt is $C_{18} H_7 O_{16} + 12 Pb O + 9 Aq$, or $C_{18} H_7 O_{16} + 3 Pb O + 9 (Pb O Aq)$.

The result of these different analyses justify, in my opinion, fully the formula which I have adopted for their expression. It might perhaps be urged that in the analysis of the silver salt, there was obtained too much carbon by 0·39 per cent., and that this

being so unusual a direction for the analysis of an organic substance to vary from the truth, a modification of the formula should be adopted. I consider, however, that where the formula gives, in the other instances, results so very consonant to experiment, there may be in that one case some little inaccuracy of weighing suspected, particularly as the excess of hydrogen is also in some degree greater than should be found in the analysis of a substance that had been so well dried.

Another reason for the adoption of the formula $C_{18}\,H_7\,O_{16}$ is, that it accounts most easily for the formation of this substance at the expense of the azolitmine; the azolitmine losing an equivalent of ammonia and gaining six equivalents of oxygen. Thus

$$\begin{array}{ll} \text{Azolitmine} \ldots & C_{18}\,H_{10}\;\;N\;\;O_{10} \\ & \underline{\quad -H_3 - N + O_6} \\ \text{Spaniolitmine} \ldots & C_{18}\,H_7 \qquad\;\; O_{16} \end{array}$$

the replacement being regular; for as the hydrogen and azote do not exist as ammonia in azolitmine, they are, although perhaps evolved as ammonia, separately replaced, the three equivalents of hydrogen making way for three of oxygen, and the nitrogen being equivalent to three equivalents of oxygen also, as has been fully proved by the Researches of LAURENT and of others. Indeed, if azolitmine be considered as the source from whence the spaniolitmine is derived, no other formula can well be taken, for any change in the number of equivalents of carbon would render the decomposition unnecessarily complicated.

If, however, the spaniolitmine be supposed to originate in the decomposition of erythrolitmine, a formula may be adopted at once deducible by the simplest considerations of substitution, and agreeing fully as well as that previously given with the analytical results. Thus

$$\begin{array}{ll} \text{Erythrolitmine} \ldots & = C_{26}\,H_{22}\quad O_{12} \\ & \underline{\quad\;\; -H_{11} + O_{11}} \\ \text{Becomes spaniolitmine} & = C_{26}\,H_{11}\quad O_{23} \end{array}$$

The calculated results of this formula I subjoin, in order that they may be compared with the experimental numbers, and with those given by the other theory.

$C_{26}\,H_{11}\,O_{23}$.			$C_{26}\,H_{11}\,O_{23} + 4\,Ag\,O$.		
C_{26} =	158·6	44·85	C_{26} =	158·6	19·40
H_{11} =	11·0	3·11	H_{11} =	11·0	1·34
O_{23} =	184·0	52·04	O_{27} =	216·0	26·42
	353·6	100·00	Ag_4 =	432·0	52·84
				817·6	100·00

These results agree better with experiment than those given by the other view, but the constitution of the purple lead salt is opposed to it, as, the organic substance in the purple lead salt being $C_{26}\,H_{11}\,O_{23}$, the oxide of lead amounts to seven and a half

equivalents, which can scarcely come within the limits of experimental error. The basic lead salt agrees well with $C_{26} H_{11} O_{23} + 16 Pb O$.

It would be very wrong, with the limited data which were in my power to obtain, to fix decidedly upon one of these formulæ to the absolute exclusion of the other. They both account for the existence of spaniolitmine completely, and the latter simply. For the elimination of the azote from bodies such as those now being described occurs but rarely, and should not consequently be supposed to occur in cases where it can be avoided. I leave, therefore, to future investigators in this field the determination of whether the equivalent of spaniolitmine should be considered $C_{18} H_7 O_{16}$, or $C_{26} H_{11} O_{23}$.

Section IV. *Of the Decolorization of the Bodies which exist in Archil and in Litmus.*

The various coloured substances which have been described in the preceding sections, will now require to be considered in some points of view, which being common in a great degree to all, would have led to useless repetition had their discussion been entered upon in the case of each individual substance. I have reserved, therefore, to the present stage of the investigation all general considerations, and shall now proceed to the examination of such points of their history as yet remain unnoticed.

The question as to whether the proper colour of litmus be red or blue, may now be considered as finally set at rest, and the theory of those changes of colour which have from so early an age in chemistry served for the recognition of alkaline or acid properties, is definitely laid down. Among the various suppositions made from time to time by chemists as to the nature of litmus, the idea of PERRETTI has ultimately been proved to be the most correct, although, as his views were not supported by any accurate experiment, no positive value could be attached to his opinion. Litmus is reddened by acids, because these acids remove the loosely combined ammonia by which the blue colour is produced, and the so-called hydrogen acids liberate the colouring matter, inasmuch as they combine with the alkali to form bodies (chlorides or iodides) with which the colouring matter has no tendency to unite. Thus the mysterious reddening of litmus paper, by which so many chemists of narrow ideas imagined that the most cogent philosophical proofs of the basic power of the compounds of hydrogen might be evaded, is found to be merely produced by the chloride of hydrogen, &c. forming on potash chloride of potassium, and with ammonia sal-ammoniac, and the proper red colouring matter becoming free. It is thus sufficiently shown that the reddening of litmus is no proof that chloride of hydrogen is an acid, but that the double decomposition which occurs is the same in principle, whether hydrogen or a fixed metal come into play, thus taking azolitmate of ammonia and chloride of hydrogen upon the one hand, and azolitmate of ammonia and chloride of copper on the other; the decompositions are

first, $(C_{18} H_{10} N O_{10} + N H_4 O) + Cl H. = (C_{18} H_{10} N O_{10} + H O) + Cl N H_4$;

and second, $(C_{18} H_{10} N O_{10} + N H_4 O) + Cl Cu = (C_{18} H_{10} N O_{10} + Cu O) + Cl N H_4$.

The bodies $C_{18} H_{10} N O_{10} . H O$, and $C_{18} H_{10} N O_{10} . Cu O$, differ in solubility and colour, but are generated by reactions identical so far as principle is concerned.

Are the coloured substances in archil and litmus themselves acids? This is a question which I consider as being of very little consequence to science, particularly as the word acid has by the progress of research been deprived of almost all definite meaning in philosophic language, and can scarcely be used except for purposes of familiar illustration. These various substances do not redden litmus, but if browned turmeric paper be brought into contact with one of the red litmus bodies, the alkali is divided between the red and the yellow material, and the browning of the one diminishes according as the other becomes blue. Whichever colouring matter is in excess preponderates, and hence I consider that the usual characters of acidity are so slightly marked, as to render it more suitable to adopt the indifferent termination in *ine*, which I have used for all of the substances described in this paper except one. This is the erythroleic acid, and if chemists approve of the mode of distinction proposed for the two orceines, I should prefer indicating the difference between the erythroleins in a similar way. The erythroleic acid should then be beterythrolein, and the other alpherythrolein. Whatever nomenclature chemists in general may adopt, I shall myself willingly accede to.

One of the most singular and obscure properties of these colouring matters, is that of becoming colourless under a variety of circumstances, and of generating a series of compounds, which are white whilst they remain unchanged, but which, on exposure to the air, become coloured, and assume their original condition. These effects may be produced in many ways, of which I shall notice the more important.

It is long known that sulphuretted hydrogen possesses the property of blanching litmus, but chemists are not agreed as to the precise manner in which it takes place. Some refer it to a deoxidation effected by the hydrogen, like that which the same gas produces on salts of the peroxide of iron; others, and as I have found more accurately, look upon the sulphuretted hydrogen as combining unaltered with the colouring material; these chemists being, however, in error in supposing the colouring matter to be blue. The grounds on which I base my opinion of the nature of this phenomenon are the following.

First. If a perfectly clear solution of an alkaline salt of a litmus or archil body be treated with pure sulphuretted hydrogen, a colourless and scarcely opalescent liquor is obtained, the quantity of sulphur deposited being nothing, or almost inappreciable. This liquor contains an alkaline sulphuret, as may be proved by its action on a salt of iron or of manganese. If it be boiled, the sulphuretted hydrogen is given off, and the liquor becomes reddish, but very long boiling, or else exposure to the air, is necessary, that it may become fully red. It cannot be completely restored to its original blue or violet colour without the addition of some more alkali. Taking azolitmine as the standard, the reaction evidently is

$$C_{18} H_{10} N O_{10} . N H_3 + 2 S H = C_{18} H_{10} N O_{10} . H S + S N H_4.$$

Second. If a solution of persulphuret of calcium or of sulphuret of barium be mixed with a solution of a blue litmus liquor, no loss of colour results. Some blue azolitmate of lime or of baryta is deposited, but no decolorization occurs. On the addition of an acid, there is an immediate disengagement of sulphuretted hydrogen, and the blue colour at once disappears.

Third. If azolitmate of lead be treated by a current of sulphuretted hydrogen, it is converted into a black powder undistinguishable in colour from sulphuret of lead. This powder may be boiled in water without being decomposed, but by protracted boiling or washing it yields azolitmine, though very sparingly. When treated with solution of potash or ammonia, a deep blue liquor is immediately obtained, and sulphuret of lead remains behind. It is, therefore, a positive chemical compound of azolitmine and sulphuret of lead corresponding to that containing the oxide of that metal; thus

$$C_{18}H_{10}NO_{10} + 3\,PbO \text{ is similar to } C_{18}H_{10}NO_{10} + 3\,PbS.$$

This black substance cannot be azolitmine precipitated and mixed mechanically with sulphuret of lead, for water of sulphuretted hydrogen dissolves azolitmine better than pure water. In this compound also the colour of the azolitmine is completely lost, as when it combines with sulphuretted hydrogen in solution.

Fourth. If in place of azolitmine the betaorceine in combination with oxide of lead be acted upon by sulphuretted hydrogen, the evidence is perfectly decisive that the black substance produced is a compound of orceine and sulphuret of lead. It may be boiled in alcohol without yielding up a trace of colouring matter, but when treated with water of ammonia it is immediately decomposed, the usual rich purple liquor being produced. It is remarkable, however, that an excess of sulphuretted hydrogen has, on the betaorceinate of lead, the same effect which ammonia would have, that is, to produce a more basic salt. Thus if the betaorceinate of lead be diffused through water and treated with sulphuretted hydrogen, a considerable quantity of betaorceine will be found in the colourless liquor combined with sulphuretted hydrogen, the reaction being

$$2\,(C_{18}H_{10}NO_8 . 3\,PbO) + 7\,SH = C_{18}H_{10}NO_8 . 6\,PbS + C_{18}H_{10}NO_8 . HS.$$

Fifth. A point of considerable interest as involved in the action of sulphuretted hydrogen on these colouring matters, is to ascertain whether in the decolorized form there might not be a certain quantity of the oxygen of the substance replaced by sulphur. Thus, that from $C_{18}H_{10}NO_{10} + SH$ there might be formed $C_{18}H_{10}NO_9S + HO$. That this does not take place, is fully shown by the constitution of the compounds with the metallic sulphurets. On destroying, by means of nitric acid, the compounds of betaorceine and of azolitmine with sulphuret of lead, I found that neutral sulphate of lead was formed, and that the liquors contained no trace of sulphuric acid. The sulphur was, therefore, only in sufficient quantity to convert the lead into sulphuret, and hence the oxygen of the organic substance is not in any degree replaced by sulphur.

It results from these experiments, that precisely as the colouring matters combine with water to form different shades of red coloured bodies—with ammonia (amidide of hydrogen) to produce a series of bodies which are blue or purple—so they combine with sulphuret of hydrogen to form colourless compounds in solution, which, if solid, would very probably be white. I attempted frequently to obtain these compounds solid, but without success, the sulphuretted hydrogen escaping at ordinary temperatures, and the substance being soluble both in water and in spirit, rendered my trials useless. The equivalency of these three series of bodies is evident, however, when we compare

$$C_{18}\,H_{10}\,N\,O_{10}+H\,O$$
$$C_{18}\,H_{10}\,N\,O_{10}+H\,Ad$$
$$C_{18}\,H_{10}\,N\,O_{10}+H\,S.$$

The similarity of character which pervades oxygen, amidogene, and sulphur is manifest in other departments of organic chemistry; precisely therefore as these colouring matters combine with metallic oxides and metallic sulphurets, so may we expect to discover at some future period, bodies consisting of them in union with metallic amidides.

In addition to the action of sulphuretted hydrogen, the colouring matters of litmus may be blanched by other deoxidizing agents of a very distinct character, and whose action it will be of the highest interest to be able to study in detail. It had been long known that by means of nascent hydrogen, the colours of a great variety of flowers might be removed, and I have found that in this way all the various colouring substances of litmus and of archil may be rendered white, and converted into new bodies, an exact examination of which is very difficult. The coloured bodies may also be reduced to the white condition by means of those metallic oxides which powerfully attract oxygen, as the protoxides of tin and iron, and in these white conditions they combine with the various bases to form salts or lakes, which on exposure to the air, rapidly become red or purple. In all these cases the reaction appears at first sight almost necessarily to consist in the removal of oxygen, but it will be found that there is very full evidence against that opinion, and that in reality the change results from the addition of a certain quantity of hydrogen to the substance. These white substances I propose to indicate by the initial word Leuco (from λευκος, *white*), and there is no doubt but there exists one for each coloured matter, but I have only obtained numerical or exact results with two, the leucolitmine formed from azolitmine, and the leucorceine formed from the betaorceine.

When a solution of orceine in water of ammonia is rendered slightly acid by muriatic acid, and a slip of zinc immersed in it, the liquor becomes after some time perfectly colourless, but recovers its original red tinge rapidly when exposed to air. If to the colourless solution water of ammonia be added, a copious white precipitate is produced, which very soon becomes pink, and ultimately purple, on exposure. To

examine this precipitate in its white form, it was immediately, on being formed, thrown upon a filter and placed under the receiver of an air-pump, from which the air was removed, and then it was filled with carbonic acid gas. As soon as the liquor had filtered through, the filter was filled with warm distilled and recently boiled water, and the replacement of the air, by carbonic acid gas, again proceeded with. This was continued until the substance was found to have been washed enough.

A dish of oil of vitriol was then placed under the receiver, and the vacuum maintained until the precipitate had become completely dry. In no case did I succeed in obtaining the precipitate white when dry. Most frequently it was spoiled altogether, becoming purple. But in a case where I obtained it of a uniform pale pink colour, it was analysed.

0·451 gramme of substance gave, by ignition until all organic matter was burned off, then moistening with nitric acid, and again igniting, 0·157 of oxide of zinc.

0·382 gramme of substance gave 0·439 of carbonic acid, and 0·160 of water.

The formula resulting is $C_{18}\,H_{14}\,O_{10}\,N + 3\,Zn\,O$, by which the numbers obtained are

	Theory.		Experiments.
18 Carbon . .	109·8	32·41	31·80
14 Hydrogen .	14·0	4·13	4·66
1 Nitrogen . .	14·1	27·77	28·73
10 Oxygen . .	80·0		
3 Oxide of zinc	120·9	35·69	34·81
	338·8	100·00	100·00

This formula may be rationally assumed as either $C_{18}\,H_{10}\,N\,O_6 + 3\,Zn\,O + 4\,H\,O$, or $C_{18}\,H_{12}\,N\,O_8 + 3\,Zn\,O + 2\,H\,O$, the decolorized condition being supposed due to either a loss of oxygen or gain of hydrogen. In order to compare it with the ordinary betaorceinate of zinc, a specimen of fine purple salt was analysed. It had been carefully dried at 212° FAHR.

0·982 gramme gave, by ignition and treatment with nitric acid, 0·331 of oxide of zinc.

0·651 gramme gave 0·235 of water, and of carbonic acid 0·720.

The resulting formula is $C_{18}\,H_{14}\,N\,O_{12} + 3\,Zn\,O$, from which result the numbers:

	Theory.		Experiment.
18 Carbon . .	109·8	30·95	30·53
14 Hydrogen .	14·0	3·95	4·02
1 Nitrogen . .	14·1	31·03	31·73
12 Oxygen . .	96·0		
3 Oxide of zinc	120·9	34·07	33·72
	354·8	100·00	100·00

This formula, $C_{18} H_{10} N O_8 + 3 Zn O + 4$ aq, is completely analogous to that of the betaorceinate of copper, which was found to be $C_{18} H_{10} N O_8 + 3 Cu O + 4$ aq.

The white orceinate of zinc differs from the purple variety in containing two equivalents of oxygen less, but the above analyses cannot be considered as fully deciding whether the substance in an anhydrous form is expressed by the formulæ $C_{18} H_{12} N O_8$, or $C_{18} H_{10} N O_6$. To obtain more complete evidence, leucorceinate of zinc (the same specimen as that analysed) was exposed in LIEBIG's apparatus to a stream of dry carbonic acid in an oil bath, heated to 280° of FAHR., until long after all traces of water had passed away, and the bulb-tube containing the substance had ceased to lose weight. In this experiment 0·547 of material gave 0·030 of water, being 5·48 per cent., and the remaining 0·517 gave, by careful ignition until all organic matter was removed, moistening with nitric acid, and ignition a second time until all traces of nitrous fumes were driven off, 0·193 gramme of oxide of zinc, corresponding to 35·39 per cent. Taking the dry leucorceine as $C_{18} H_{10} N O_8 + 2 H$, the numbers are

	Theory.		Experiment.
1 Leucorceine	199·9	59·00	59·13
2 Water . .	18·0	5·31	5·48
3 Oxide of zinc	120·9	35·69	35·39
	338·8	100·00	100·00

The quantity of oxygen separable in the form of water, is therefore fully shown to be two equivalents, and hence the formation of the leucorceine is due to the fixation of hydrogen in the new body, and not to the abstraction of oxygen from the old.

When a solution of protochloride of tin is added to azolitmine dissolved in water of ammonia, a fine purple precipitate falls, which having been well washed and dried in a temperature of 212° in LIEBIG's apparatus, was analysed as follows.

0·547 gramme ignited and treated with nitric acid, as in former instances, gave 0·231 of peroxide of tin.

0·631 gramme gave 0·202 of water, and 0·681 of carbonic acid.

The formula deducible from these results is $C_{18} H_{12} N O_{12} + 2 Sn O$, this salt containing only one half of the protoxide of tin existing in the protazolitmate of tin, described under the head of azolitmine. The numerical results are

	Theory.		Experiment.
18 Carbon .	109·8	30·03	29·86
12 Hydrogen	12·0	3·28	3·55
1 Nitrogen .	14·1	3·85	33·37
14 Oxygen .	112·0	30·63	
2 Tin . .	117·8	32·21	33·22
	365·7	100·00	100·00

It is probable that this azolitmate of tin may be the more definite of the two, as possibly an excess of ammonia may have produced the formation of the more basic salt formerly described. When this salt, diffused through water, is mixed with a small quantity of muriatic acid and boiled for some time, it becomes whitish or slightly fawn-coloured, and the tin is found to have been changed into peroxide. A quantity of the tin makes its appearance as peroxide uncombined, but the greater part remains united with the leucazolitmine. I found the difficulties of procuring this compound in its white form proper for analysis, to be insuperable. Even in the best exhaustions I could produce, it gradually became red; and when exposed even for a short time to the air, it forms a bright scarlet lake, remarkably distinct from that produced by the protoxide of the same metal. I consequently was not able to analyse the leucazolitmate of tin, or to obtain at all the same evidence concerning it that I did with regard to leucorceine.

I allowed a quantity of leucazolitmate of peroxide of tin diffused through water, to lie exposed to the air in a flat dish until it was completely converted into the scarlet substance. This was then dried at 212° and analysed, there being some peroxide of tin mechanically diffused through it, but not much.

0·652 gramme gave water 0·215, and 0·658 of carbonic acid.

1·107, by ignition and treatment with nitric acid, gave 0·443 of peroxide of tin.

The resulting formula is $C_{18}\ H_{12}\ N\ O_{16}\ Sn_2$, giving

	Theory.		Experiment.
18 Carbon .	109·8	28·77	27·93
12 Hydrogen	12·0	3·14	3·66
1 Nitrogen .	14·1	3·69	36·93
16 Oxygen .	128·0	33·54	
2 Tin . .	117·8	30·86	31·48
	381·7	100·00	100·00

This salt, exposed to a temperature of 280° in an oil bath, loses 4·5 of water or two equivalents, and hence when dry is $C_{18}\ H_{10}\ N\ O_{10} + 2\ Su\ O_2$.

The blanching of azolitmine by hydrogen can easily be effected by precisely the same means as were described under leucorceine, but the restoration of the colour occurs so rapidly and from such slight access of air, that it must be considered as still more difficult to isolate the white condition than the orceine. I consequently was not able to analyse the leucazolitmate of zinc, and the proofs of its being similar in constitution to leucorceine must rest on analogy alone.

An additional reason for looking on these bodies as being produced by the addition of hydrogen and not by the abstraction of oxygen, is the fact, that where there are so many formed by the absorption of oxygen from the same source, the subsequent removal of oxygen should regenerate the bodies lower in the scale, in place of produ-

cing a series of new bodies totally different in colour. Thus, as by exposure to oxygen, there are produced

$$\left.\begin{matrix} C_{18}\,H_{10}\,N\,O_5 \\ C_{18}\,H_{10}\,N\,O_8 \\ C_{18}\,H_{10}\,N\,O_{10} \end{matrix}\right\} \text{ and } \left\{\begin{matrix} C_{26}\,H_{22}\,O_4 \\ C_{26}\,H_{22}\,O_8 \\ C_{26}\,H_{22}\,O_{12} \end{matrix}\right.$$

so by exposure to hydrogen, the same series should be re-produced in the inverse order, if it act only by removing oxygen. This, however, does not take place; on the contrary, it appears that as from $C_{18}\,H_{10}\,N\,O_8$, there is formed by oxygen $C_{18}\,H_{10}\,N\,O_{10}$, so there is by hydrogen $C_{18}\,H_{10}\,N\,O_8\,H_2$, and perhaps from $C_{18}\,H_{10}\,N\,O_5 \,.\, C_{18}\,H_{10}\,N\,O_5 \,.\, O_3$, and $C_{18}\,H_{18}\,N\,O_5 \,.\, H_3$, and from $C_{18}\,H_{10}\,N\,O_{10}$ hydrogen forms $C_{18}\,H_{10}\,N\,O_{10}\,H$. I conceive that in this way alone can a satisfactory explanation of all the facts be given. That deoxidation is not the characteristic process, obtains also probability from the fact, that neither sulphurous acid, nor a solution of a sulphite, has any effect upon azolitmine, either free or in alkaline combination. The sulphurous acid reddens litmus as any other acid, but has no power whatsoever to remove its colour.

There is no circumstance, in the history of the colouring bodies, of more interest than that of the bleaching powers of chlorine; whether considered as affording the theory of a process, so long and so deservedly esteemed one of the most important applications of chemistry to the arts, or examined with regard to testing by its means the generality and exactness of the important views recently deduced, concerning the constitution of organic bodies, from the results of the action of chlorine upon them, by studying in a new class of substances, how far the principle on which it acts may be modified or confirmed. Before the study of organic chemistry had attained the accuracy which it now possesses, chlorine was considered to bleach by decomposing water, with the hydrogen of which it entered into combination. The oxygen being thus set free, was supposed to act in its nascent form with peculiar power upon the colouring matter, and thus to produce in a few minutes the same effect as should have resulted, though much more slowly, from the action of air and moisture. When the action of chlorine on organic substances became more minutely studied, it was found that a portion of chlorine entered into the constitution of the new substance formed by its action, and it was natural to suppose that such should be the case in bleaching also. This idea appears to have been first distinctly advanced by ROBIQUET in the article Blanchiment, in the Dictionnaire Technologique, in 1823; but as he did not rest it on any experimental evidence, it did not attract attention, and I was not aware that the true theory of bleaching had been suggested by that chemist until these researches were almost quite complete.

In addition to the principle of the fixation of chlorine in the resulting compound, there is another point to be attended to in researches like the present, and which will be found of high interest in a theoretical point of view. In the generality of organic bodies, the fixation of chlorine is accompanied by loss of hydrogen, usually to an

equivalent amount, and it is known that on this principle is founded the law of substitutions, proposed by DUMAS, and which has led that illustrious chemist to his theory of organic types, which now occupies so much the minds of chemists. Now it is a question, does this replacement of hydrogen occur in bleaching? are the colouring matters similar to other organic substances in that respect? or do they, particularly when containing azote, follow other and peculiar laws? To the solution of these questions, the following experiments were directed.

1st. Action of chlorine on betaorceine.

When chlorine is brought into contact with pure betaorceine, diffused through water, or still better, in solution in an ammoniacal liquor, the colour gradually alters until the whole is changed into a brownish yellow substance insoluble in water. To this substance I give the name of *Chlororceine*. As soon as all the orceine is decomposed, the current of chlorine should be stopped, as by a great excess of chlorine the composition of this body is subject to be altered. The chlororceine is insoluble in water; soluble in alcohol and ether; also in water of ammonia, forming a deep yellowish brown liquor, from which it is again precipitated by acids, though not without being changed. This ammoniacal liquor is also precipitated by metallic salts, forming compounds which probably contain some form of chlororceine, but which have not been more minutely examined.

The chlororceine, simply prepared and dried at 212° FAHR., was analysed.

A. 0·700 of material gave by ignition with carbonate of soda, and precipitation with nitrate of silver, 0·766 of chloride of silver.

0·576 of material gave 0·227 of water, and 0·842 of carbonic acid.

Another specimen being examined,

B. 0·842 gramme gave 0·887 of chloride of silver.

0·543 gramme gave 0·782 of carbonic acid, and 0·210 of water.

Hence the composition in 100 parts.

	A.	B.	
Carbon	40·35	39·82	100·00
Hydrogen	4·38	4·31	
Oxygen and Nitrogen	28·27	29·87	
Chlorine	27·00	26·00	

The formula $C_{18} H_{10} NO_8 Cl_2$, gives

18 Carbon	109·8	40·86
10 Hydrogen	10·0	3·72
8 Oxygen	64·0	29·07
1 Nitrogen	14·1	
2 Chlorine	70·8	26·35
	268·7	100·00

In the production of this substance there are therefore two equivalents of chlorine directly added to the betaorceine, and the proportion of hydrogen proves that in this case no replacement of hydrogen occurs. This is further shown by the fact, that in the action of chlorine on pure orceine, there is produced a mere trace of hydrochloric acid. The relation of the carbon and the nitrogen has been assumed as being unaltered by the action of the chlorine: this I have not directly proved completely; indeed, for some time I believed that a portion of the nitrogen was eliminated by the chlorine, as sal-ammoniac, but although the small quantity of orceine at my disposal prevented me from fully ascertaining the relation to remain eighteen to one, yet in a trial which I made it appeared so nearly that, that I believe it may be looked upon as sufficiently determined to be made the basis of the formula. I therefore look upon chlororceine as being $C_{18}\,H_{10}\,N\,O_8\,Cl_2$, and I consider the bodies

Azolitmine . .	$C_{18}\,H_{10}\,N\,O_8 . O_2$
Leucorceine . .	$C_{18}\,H_{10}\,N\,O_8 . H_2$
Chlororceine . .	$C_{18}\,H_{10}\,N\,O_8 . Cl_2$

as being similar to one another, and belonging to the same family or organic type.

It is evident that the betaorceine itself might be looked on as a sort of compound radical, of which the azolitmine would be the oxide, and the others respectively the hydruret and chloride. Thus calling betaorceine, from its purple colour, Phœnyl. = Phy.

Azolitmine becomes . . .	$Phy + O_2$
Leucorceine.	$Phy + H_2$
Chlororceine	$Phy + Cl_2$.

It is adverse to this view, that the bodies, which we consider to be compound radicals, do not possess the property of combining with metallic oxides, as orceine has been found to do. The action of alkalies on chlororceine is also opposed to this simple view.

When chlororceine is dissolved in solution of potash, or of ammonia, there is formed a certain portion of metallic chloride, and on the addition of an acid, a substance is precipitated rather darker coloured than the chlororceine had been originally, but otherwise identical with it in properties. In composition, this substance differs remarkably from chlororceine; the proportion of chlorine remaining in it is not always the same, the chlororceine appearing to dissolve at first without alteration, but by boiling for some time, being decomposed in a complex manner, giving an alkaline chloride and two organic substances, which differ in solubility, though not very much. On this account, the analyses made of this precipitated substance do not agree well among themselves, and I shall here introduce the analysis of a specimen in which the decomposition appeared to be most complete, only for the purpose of pointing out the direction of the result, and perhaps its approximate value. It was the more soluble portion which was analysed.

0·525 gramme, dried at 212°, gave 0·200 of water, and 0·788 of carbonic acid.
1·225 gave 0·653 of chloride of silver.

These results are expressed by the formula $C_{18}\ H_{10}\ N\ O_{12}\ Cl$, the numbers being

	Theory.		Experiment.
18 Carbon. . .	109·8	41·38	41·51
10 Hydrogen. .	10·0	3·77	4·23
1 Nitrogen . .	14·1	41·50	41·11
12 Oxygen . .	96·0		
1 Chlorine . .	35·4	13·35	13·15
	265·3	100·00	100·00

It is not easy to see how this compound arises directly from the chlororceine, and it can only be in virtue of a very complex decomposition. The portion, which dissolves less easily in water of ammonia, not having been analysed, its constitution can only be surmised. If all the chlorine had been removed by the alkali, and replaced by oxygen, it is evident that azolitmine should be produced, which is certainly not the case; and I hence consider that by the action of the alkali one half of the chlorine is removed, and a substance generated, expressed by the formula $C_{18}\ H_{10}\ N\ O_9\ Cl$, which being subsequently decomposed by the excess of alkali may be supposed to break up into $C_{18}\ H_{10}\ N\ O_6\ Cl$, and $C_{18}\ H_{10}\ N\ O_{12}\ Cl$, of which the latter is that analysed. I throw out this suggestion without attaching much weight to it, for although it is not likely that the true theory is far from that now described, yet the study of this reaction is of course very incomplete.

Action of Chlorine on Azolitmine.

By the action of chlorine on azolitmine, there is produced a peculiar yellow substance, insoluble in water, soluble in alcohol and ether; soluble also in alkalies, from whence it is precipitated unchanged by the addition of an acid. It is capable of uniting, by means of double decomposition, with metallic oxides and forming salts. The name of chlorazolitmine may be applied to it.

Its analysis gave the following results:

A. 0·217 gramme gave 0·123 chloride of silver.
0·314 gramme gave 0·498 of carbonic acid, and 0·133 of water.

B. 0·859 of another portion, dried at 212° FAHR., gave 0·511 of chloride of silver.
0·535 gramme gave 0·834 of carbonic acid, and 0·221 of water.

The composition in 100 parts is hence

	A.	B.	
Carbon	43·95	43·13	100·00
Hydrogen	4·70	4·59	
Oxygen and Nitrogen . .	37·39	37·60	
Chlorine	13·96	14·68	

Whence the formula $C_{18} H_{10} N O_{10} Cl$; and the reaction appears to be extremely simple, consisting in the addition of an equivalent of chlorine without any elimination of hydrogen. The numbers deduced from the formula are

18 Carbon. . .	109·8	44·04
10 Hydrogen. .	10·0	4·01
1 Nitrogen . .	14·1	37·75
10 Oxygen . .	80·0	
1 Chlorine . .	35·4	14·20
	249·3	100·00

The leucazolitmine, if it could have been analysed in a pure condition, would very probably have been found similar in constitution to chlorazolitmine. The bodies $C_{18} H_{10} N O_{10} . H$., and $C_{18} H_{10} N O_{10} . Cl$ being to each other as $C_{18} H_{10} N O_8 . H_2$, and $C_{18} H_{10} N O_8 . Cl_2$.

Action of Chlorine on Erythrolitmine.

When erythrolitmine is diffused through water, and a current of chlorine passed through it, it changes into a buff-coloured substance, which is insoluble in water, and resembles all the other bodies, formed by the decolorizing action of chlorine upon these colouring matters, in its general properties. It may be termed chlorerythrolitmine, and was analysed after having been dried at 212° in LIEBIG's apparatus.

A. 0·412 gramme gave 0·118 of chloride of silver.

0·433 gramme gave 0·896 of carbonic acid, and 0·318 of water.

B. 0·732 of another specimen gave 0·197 of chloride of silver.

0·365 gave 0·759 of carbonic acid, and 0·270 of water.

The resulting composition per cent. is

	A.	B	
Carbon. . . .	57·24	57·51	100·00
Hydrogen. . .	8·15	8·22	
Oxygen. . . .	27·56	27·62	
Chlorine . . .	7·05	6·65	

Hence results the formula $C_{52} H_{44} O_{19} Cl$, giving

52 Carbon. . . .	317·2	57·82
44 Hydrogen . . .	44·0	8·02
19 Oxygen. . . .	152·0	27·71
1 Chlorine . . .	35·4	6·45
	548·6	100·00

This result is very singular, inasmuch as the chlorine compound contains less oxygen than that from which it had been formed, and also that two equivalents of erythrolitmine are involved in the decomposition which fixes one of chlorine. This may

be, however, in great part explained by the fact, that at the same time with the chlorerythrolitmine there is produced another body, soluble in water, but which I have not yet obtained in a form proper for analysis. On this soluble substance I consider the oxygen lost by the chlorerythrolitmine to be fixed; and although it has not as yet been analysed, an idea of its probable constitution may be formed, if we consider it to be produced as follows:

Three equivalents of erythrolitmine . . .	$C_{78}\ H_{66}\ O_{36}$
One equivalent of chlorine	Cl

may be considered to produce

One equivalent of chlorerythrolitmine . .	$C_{52}\ H_{44}\ O_{19}\ Cl$
One equivalent of soluble substance . . .	$C_{26}\ H_{22}\ O_{17}$

It is possible that this soluble substance may contain in addition a quantity of chlorine.

The chlorerythrolitmine itself I conceive to be a compound of unaltered erythrolitmine, with the true chlorine substance. Thus

True chlorine body. . . .	$C_{26}\ H_{22}\ O_{7}\ Cl$
Erythrolitmine	$C_{26}\ H_{22}\ O_{12}$
Actual chlorerythrolitmine .	$C_{52}\ H_{44}\ O_{19}\ Cl.$

The true erythrolitmine is thus indicated to be erythroleic acid, in which an equivalent of oxygen is replaced by chlorine, $C_{26}\ H_{22}\ O_8$ resembling $C_{26}\ H_{22}\ O_7\ Cl$.

The very small quantity of chlorine which exists in chlorerythrolitmine, renders it exceedingly difficult to say, from analysis, whether hydrogen is removed or not. I do not consider myself justified in believing any loss of hydrogen to occur, in the absence of proof that it has occurred, particularly as in the other cases of the colouring matters now examined, it positively does not take place.

In acting on the bodies now described, it appears therefore that chlorine is subjected to conditions, different from those which determine the nature of the results with the generality of organic bodies, and that the replacement of hydrogen, so marked in other cases, does not exist in the class of substances under consideration. On the contrary, the action of the chlorine would appear to lend support to the idea, that as among inorganic bodies chlorine may combine either directly with metallic oxides, or else, in decomposing them, generate a higher degree of oxidizement and a chloride of the metal; so the colouring matters, at least those now examined, may be looked upon as being similarly affected, and that in reality the products of the bleaching energy of chlorine on a coloured substance, resemble in constitution the compounds of chlorine which possess bleaching powers. Thus as $Ca\,O$. combines with chlorine, so may azolitmine; and the bodies $Ca\ O\ .\ Cl$ and $Azl\ .\ Cl$ correspond. Also, as in a peroxide some oxygen may be replaced by chlorine, as in the bodies $Pb\ O_2$ and

$PbOCl . BaO_2$ and $BaO . Cl$; so from orceine, the bodies chlororceine and azolitmine may be formed of similar constitution.

I have already pointed out my reasons for considering these different series of coloured bodies as consisting not of the same organic radicals, combined with different quantities of oxygen, but as being, though formed in succession by gradual oxidation, when once produced, independent of each other, and not reducible to any common type. I should wish to be understood, however, as not insisting positively upon any theoretical considerations regarding the internal constitution of these bodies; I have met with too many difficulties in their investigation, and have seen too often ideas which I had thought well established by one series of analyses overturned by those subsequently made, not to be fully sensible of the liability to correction, to which even my present opinions may be subject. Among substances, so numerous, so similar in properties, and so variable in constitution; in a field of investigation which for numerical or accurate purposes must be looked upon as previously unexplored, it would be inexcusable rashness and presumption in me, not to look forward to the correction of my results in many instances, by those chemists who may hereafter devote themselves to the study of this subject, or to consider these researches as being more than introductory to the more accurate and detailed examination, which the great fertility and importance of this department of chemistry deserves, and, I trust, is likely to obtain from more distinguished chemists.

Royal Dublin Society,
April 21*st*, 1840.